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A NOTE ON THE FORMATION OF QUINONES BY OXIDATIVE DEMETHYLATION AND THE EFFECT OF METHYLATING AGENTS ON THEM

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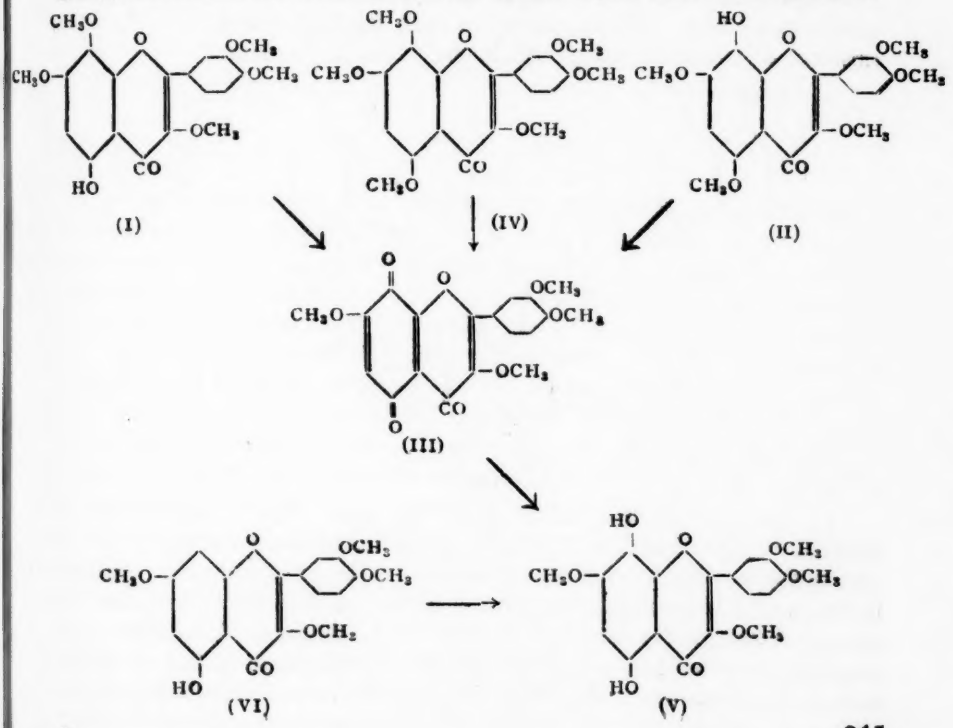
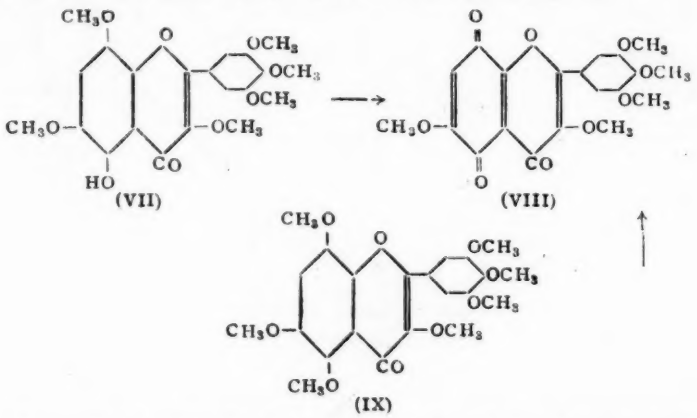
Oxidative demethylation using nitric acid has recently been found to be of great use in the study of the structure of partial methyl ethers of hydroxy flavones and also in their synthesis. This reaction was first studied in detail using compounds of the gossypetin group.[1] *O*-Pentamethyl gossypetins (I and II) having a free hydroxyl in the 5- or 8-position readily undergo this reaction to yield tetramethyl-gossypetone (III). This takes place even with gossypetin-hexamethyl ether (IV) with almost equal ease. The nature of



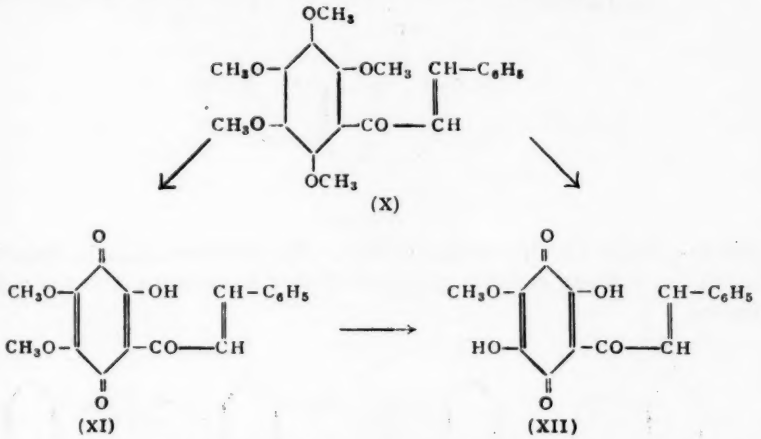
the product has been established by reduction and methylation whereby the original compound (IV) is obtained and also by comparing the quinol (V) with that formed by the nuclear oxidation of quercetin-tetramethyl ether (VI).

The above oxidative demethylation has also been studied using the dimethyl derivative of the flavone, wogonin.[2] Methoxyls para to each other are involved and no further change, either further demethylation or nuclear oxidation is found to take place. An orthodimethyl ether, 7 : 8-dimethoxyflavone has now been tested and is found to be unaffected. These experiments definitely support the explanation of the behaviour of gardenin (VII) towards nitric acid as given by Bose and Nath.[3] This reaction was originally studied by Stenhouse and Groves[4] who called the product gardenic acid. Bose and Nath showed this to be a quinone (VIII) yielding a quinol on reduction. More recently Balakrishna and Seshadri[5] have found that methyl gardenin (IX) behaves similarly and that the action of nitric acid with this substance runs a course which is quite parallel to that with gossypetin hexamethyl ether. This has therefore been taken as definite proof of the existence of two methoxyl groups in the 5- and 8-positions.



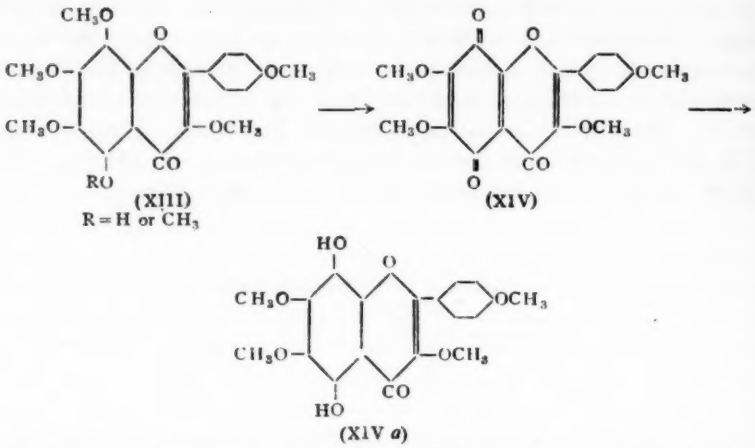
In contrast with the behaviour of the above flavone methyl ethers, pedicellin[6] (X) which is a fully methylated chalkone ether suffers further demethylation also so that the product is a hydroxy quinone. Methylpedicinin (XI) is the major first product of the reaction and in its formation three methoxyl groups are involved, two being oxidised to the quinone and the third converted into a hydroxyl group. In the course of this treatment with nitric acid some quantity of pedicinin (XII) is also formed as the result of further demethylation of a fourth methoxyl group, though for effecting

this change and getting a good yield of pedicinin final addition of alkali is better. There seems to be little doubt that the first stage is the formation of a quinone which subsequently undergoes demethylation. The ready demethylation of methoxy quinones under the influence of alkali is already known. The reaction is analogous to ester hydrolysis. From the example of the pedicellin-pedicinin change, this can obviously take place even in acid medium though it was not noted earlier in any other case.

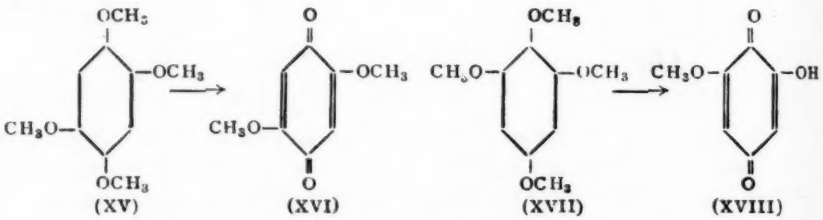


In the course of the work described in this paper certain select cases have been examined anew in order to get more information on this phenomenon and to find out what structural conditions are responsible for the differences existing between methoxy flavones on the one hand and pedicellin on the other. Among methoxy-flavones the 5: 7: 8-type (gossypetin group) and the 5: 6: 8-type (gardenin) have already been examined. As examples of the 5: 6: 7: 8-type have now been studied calycopterin-mono and dimethyl-ethers (XIII, R = H or CH_3). These include in their structures both 5: 6: 8 and 5: 7: 8-combinations and in conformity with the other flavones they undergo straightforward oxidative-demethylation to form a quinone (XIV) and no further change.

Of the simple methoxy-benzenes having para methoxyl groups the reaction of 1: 2: 4-trimethoxy benzene with nitric acid has already been studied by Schüler[7] who reported the formation a diphenyl diquinone along with some nitro compound. 1: 2: 4: 5-Tetramethoxy benzene[8] (XV) was found to behave in a simpler manner and form the dimethoxy quinone (XVI) undergoing thus only oxidative demethylation. On the other hand, 1: 2: 3: 5-tetramethoxy benzene (XVII) represents a third type yielding a

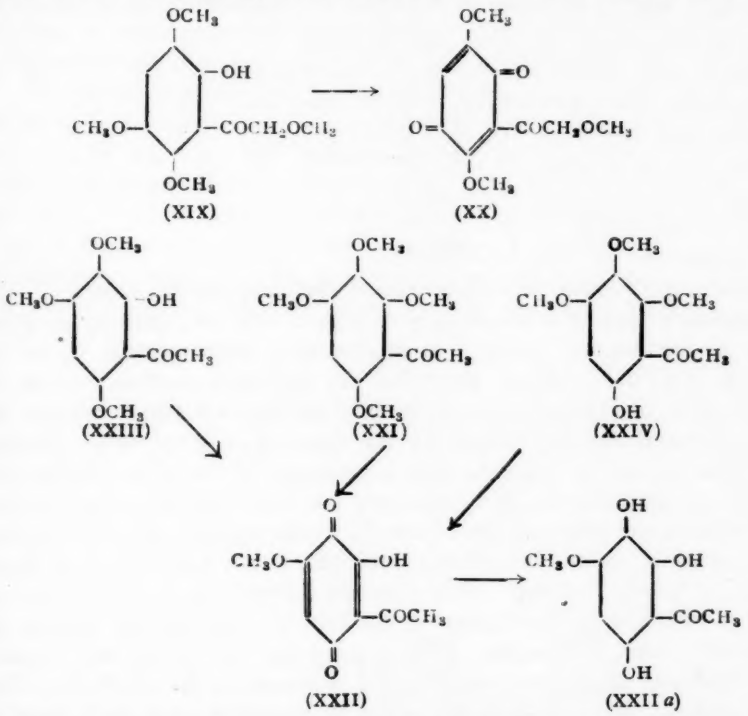


hydroxy-quinone (XVIII) as the product. This involves oxidative demethylation to the methoxy quinone stage and further demethylation to the hydroxy quinone.



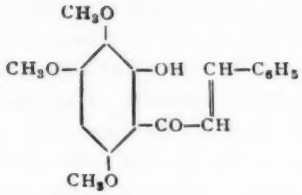
As examples of compounds more closely related to flavones and also to the chalkones, methoxy acetophenones have been chosen for study. Recently 2-hydroxy-ω: 3: 5: 6-tetramethoxy acetophenone (XIX) which is a product of fission of methyl gardenin has been studied by Balakrishna and Seshadri[5] and they have recorded that it forms a trimethoxy quinone (XX) undergoing simple oxidative demethylation just as the related 1: 2: 4: 5-tetramethoxy benzene. On the other hand, 2: 3: 4: 6-tetramethoxy acetophenone (XXI) yields a hydroxy quinone (XXII) under the same conditions. In this reaction three methoxyl groups undergo removal, two of them yielding place to the quinone structure and the third being converted into a hydroxyl The location of the hydroxyl as ortho to the ketonic carbonyl is indicated by the prominent ferric chloride colour. This inference is supported by its independent preparation from 2-hydroxy-3: 4: 6-trimethoxy acetophenone (XXIII). Even the isomeric 2-hydroxy-4: 5: 6-trimethoxy acetophenone (XXIV) yields the same product. All these reactions are correctly explained

by (1) oxidative demethylation involving the para substituted positions and (2) further demethylation of an ortho methoxyl if it should be present. The following formulæ explain the changes. It should be noted that these three ketones are derivatives of 1:2:3:5-tetramethoxy benzene. Thus there is some correlation between the behaviour of methoxy benzenes and the derived acetophenones. However, explanation of this marked difference in the behaviour of these two types of methoxy-benzene derivatives is not clear.



The important point to be noted in the above reactions with the ketones is the second stage demethylation taking place in the position ortho to the ketonic carbonyl group, the one in the para position being left out. It is of significance in the interpretation of the conversion of pedicellin into methyl-pedicinin and pedicinin.

In the next stage of our study 2-hydroxy-3:4:6-trimethoxy chalkone (XXV) and its fully methylated ether (XXVI) were found to behave very similar to pedicellin, a hydroxy quinone (XXVII) being produced as the product.



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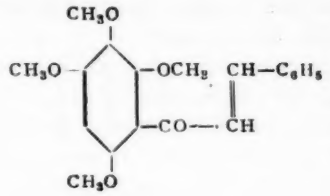

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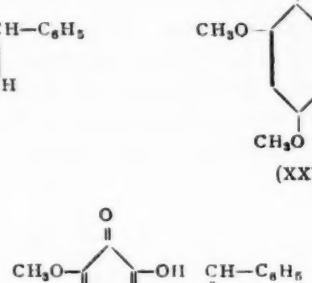
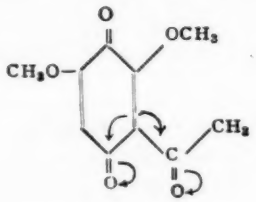


(XXVII)

With regard to the above ketones and chalkones derived from 1: 2: 3: 5 tetramethoxy benzene it is necessary to explain why the particular methoxyl ortho to the ketonic carbonyl is preferentially demethylated. From the formula (XXVIII) it will be clear that this particular position receives the double effect of the quinone and the ketonic carbonyl groups whereas the other methoxyl can be affected by the quinone carbonyl only. Another point that should be noted is that compounds of the type (XXIX), *i.e.*, hydroxy quinone ketones, give prominent red ferric chloride colour in alcoholic solution and differ markedly from the simpler hydroxy quinones (XVIII). Ferric chloride colour is generally attributed to the presence of chelation between a ketonic carbonyl and a phenolic hydroxyl in the ortho position and it is favoured by the existence of the benzene double bond between the concerned groups. In the case of the hydroxy-quinone-ketones though there is no benzenoid structure a double bond is present in the required position all the same. But this chelation seems to be rather weak since hydroxy quinone-ketones are still readily soluble in sodium bicarbonate.



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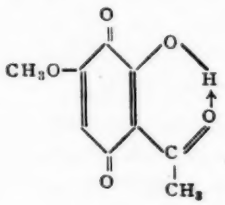
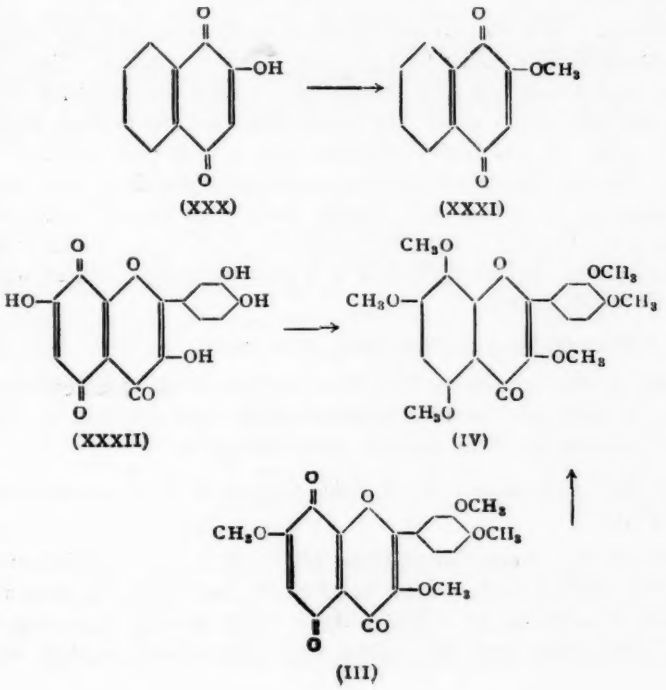


(XXIX)

Methylation of quinones

The methylation of hydroxy-quinones is not invariably successful. Only in favourable cases can it be carried out satisfactorily; an example described here is the methylation of lawsone (XXX). It was originally done by means of methyl alcohol and hydrogen chloride. The methyl ether (XXXI) has now been made easily using dimethyl sulphate and potassium carbonate in acetone medium and heating for a restricted period. The cause of failure in other cases and of the general difficulty experienced, is to be attributed to the readiness with which quinones undergo other changes. In a few of the cases studied by us it has been possible to isolate minor quantities of crystalline compounds identified as the methyl ethers of the corresponding quinols. For example from the methylation of gossypetone (XXXII) has been isolated gossypetin hexamethyl ether (IV). In this case after the methylation of the hydroxyl groups further change sets in which results in the formation of the above hexamethyl ether besides amorphous and complex products. This is supported by the fact that tetramethyl gossypetone (III) itself behaves similarly under the above conditions.



The explanation of the above reaction requires the dismutation of the methoxy quinone involving self-hydrogenation and dehydrogenation. The former gives rise to the quinol which undergoes further methylation and the latter results in polymerisation and related changes. The simplest example, quinone itself forms quinol dimethyl ether under these conditions.

That benzoquinone forms quinol as one of the products of decomposition in the presence of alkali has been observed by a number of workers in the past (see Erdtman[9]). This change is conveniently shown by the preparation of the benzoate and methyl ether of quinol from the alkaline solution. This reaction seems to be more general since it is found that gossypetone tetramethyl ether (III) yields the corresponding quinol (V) by short treatment with dilute aqueous potash. It could obviously take place even in the presence of potassium carbonate because as mentioned above the quinol methyl ethers are formed when the quinones are subjected to methylation.

Experimental

Oxidation of calycopterin dimethyl ether to 3:6:7:4′*-tetramethoxy-flavoquinone* (*XIV*)

Nitric acid (d. 1·25; 10 c.c.) was added to finely powdered calycopterin dimethyl ether (XIII, R = CH_3) (0·5 g.) with vigorous stirring. The solid assumed an orange colour and soon changed into a dark red semisolid mass. The temperature was kept at 15–20° for 15 minutes when the product became a definite red solid. It was filtered, washed with a little nitric acid of the same density followed by excess of water. When crystallised twice from benzene it appeared as orange red needles melting at 194–95°. (Found: C, 61·0; H, 4·0; $C_{19}H_{16}O_8$ requires C, 61·3; H, 4·3%.) Yield, 0·3 g. It dissolved in aqueous sodium hydroxide to a greenish brown solution which changed to yellowish brown.

Oxidation of 4′*-O-methyl-calycopterin* (*XIII*, *R = H*)

The oxidation was carried out just as in the case of the dimethyl ether. The reaction was very quick and the product readily separated out as a red solid. It was identical with the quinone described above.

Reduction of the flavoquinone to 5:8*-dihydroxy*-3:6:7:4′*-tetramethoxy flavone* (*XIV a*)

A solution of the above flavoquinone (XIV) (0·3 g.) in glacial acetic acid (2 c.c.) was treated with sodium sulphite (0·5 g.) when the deep red colour immediately changed to bright yellow. After stirring for a minute, water (50 c.c.) was added and the yellow solid filtered and washed with

water. It crystallised from benzene in the form of glistening golden yellow rectangular plates, melting at 210–12°, alone or in admixture with the sample obtained by the oxidation of 5-hydroxy-3 : 6 : 7 : 4′-tetramethoxy flavone[10] with alkaline persulphate. It readily dissolved in aqueous sodium hydroxide to a bright red solution and in alcoholic solution gave a green colour with one drop of ferric chloride and with more of the reagent the colour changed to deep brown.

Oxidation of 1 : 2 : 3 : 5-*tetramethoxy benzene to* 2-*hydroxy*-6-*methoxy-quinone* (*XVIII*)

A solution of 1 : 2 : 3 : 5-tetramethoxy benzene[11] (XVII) (5 g.) in alcohol (20 c.c.) was treated with nitric acid (d. 1·25; 20 c.c.). It was cooled so that the temperature did not rise above 50° for 15 minutes and the deep red reaction mixture was diluted with a large volume of water (500 c.c.). On saturating the solution with sodium chloride and cooling, a yellow solid separated out which was filtered and washed with a little water. The filtrate on extraction with chloroform yielded some more of the solid. When crystallised from chloroform it separated in the form of pale yellow narrow rectangular plates melting at 240–45° with decomposition. (Found: C, 54·2; H, 4·2; $C_7H_8O_4$ requires C, 54·6; H, 3·9%.) It was easily soluble in alcohol and sparingly in chloroform. In aqueous sodium bicarbonate it readily dissolved to a red solution and with ferric chloride in alcoholic solution it gave a pale brown colour.

2-*Hydroxy*-4-*methoxy*-3 : 6-*quino-acetophenone* (*XXII*)

(*a*) *From* 2-*Hydroxy*-3 : 4 : 6-*trimethoxy acetophenone* (*XXIII*).—A solution of the ketone (XXIII) (1 g.) in anhydrous ether (10 c.c.) was cautiously treated with fuming nitric acid (1 c.c.). After keeping the reaction mixture overnight the ether was removed in the cold, water was added and the mixture extracted with chloroform. The chloroform extract was dried over sodium sulphate and distilled. The orange red solid left behind was crystallised from benzene when it appeared as glistening orange red micacious plates melting at 158–60°. (Found: C, 54·8; H, 4·4; $C_9H_8O_5$ requires C, 55·1; H, 4·1%.) It was easily soluble in aqueous sodium bicarbonate giving a red colour. In alcoholic solution it gave a deep red colour with ferric chloride. Yield, 0·35 g.

(*b*) *From* 2-*Hydroxy*-4 : 5 : 6-*trimethoxy acetophenone*(*XXIV*).—A solution of the above ketone (XXIV) (0·5 g.) in dry ether (5 c.c.) was treated with fuming nitric acid (1 c.c.). After keeping at the laboratory temperature for three hours the bright orange red crystals of the quinone were filtered,

washed with a little ether and distilled water. Yield, 0·35 g. It melted at 158–60° alone or in admixture with the sample obtained from 2-hydroxy-3:4:6-trimethoxy acetophenone and the properties were also identical.

(*c*) *From* 2:3:4:6-*tetramethoxy acetophenone* (*XXI*).—A solution of 2:3:4:6-tetramethoxy acetophenone (2 g.) in anhydrous ether (10 c.c.) was treated with fuming nitric acid (2 g.). On keeping overnight an orange red crystalline solid separated out in good yield. It was filtered, washed with a little ether and recrystallised from benzene when it appeared as micacious plates melting at 158–60° alone or in admixture with the quinone obtained from 2-hydroxy-3:4:6-trimethoxy acetophenone.

2:3:6-*Trihydroxy*-4-*methoxy acetophenone* (*XXII a*)

Into a suspension of the above quinone (XXII) (0·2 g.) in water (5 c.c.) a current of sulphur dioxide was passed. The quinone dissolved and very soon pale yellow crystals separated out. After filtering, washing and recrystallising from benzene the ketone appeared as rectangular plates melting at 170–71°. (Found: C, 54·9; H, 5·4; $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%.) It was easily soluble in alcohol and sparingly in benzene. In aqueous sodium hydroxide it dissolved to a deep brown solution which became colourless on shaking with air. In alcoholic solution it gave with ferric chloride a green colour which changed to brown.

Oxidation of 2-*hydroxy*-3:4:6-*trimethoxy chalkone* (*XXV*) *to* 2-*Hydroxy*-4-*methoxy*-3:6-*quino-chalkone* (*XXVII*)

A solution of 2-hydroxy-3:4:6-trimethoxy chalkone[11] (0·5 g.) in glacial acetic acid (5 c.c.) was treated with concentrated nitric acid (1 c.c.). A deep reddish brown solution resulted. After five minutes the solution was diluted with water and the orange coloured solid filtered and washed with water. Crystallisation from chloroform yielded orange red thin plates melting at 186–87°. (Found: C, 67·5; H, 4·5; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.) It was sparingly soluble in alcohol, chloroform and benzene, and readily soluble in aqueous sodium bicarbonate to a reddish brown solution. In alcoholic solution it gave a deep red colour with ferric chloride.

2:3:4:6-*Tetramethoxy chalkone* (*XXVI*)

Preparation.—A solution of 2-hydroxy-3:4:6-trimethoxy chalkone (2 g.) in acetone (25 c.c.) was refluxed with dimethyl sulphate (2 c.c.) and potassium carbonate (10 g.) for 12 hours. The solvent was distilled off, the residue treated with water and extracted with ether. On evaporating off the ether a very pale yellow oily liquid was left behind which did not crystallise even on keeping for a long time. It was insoluble in aqueous sodium hydroxide

and gave no colour with ferric chloride. It was therefore directly employed for oxidation.

Oxidation.—A solution of the tetramethoxy chalkone (1 g.) in glacial acetic acid (3 c.c.) was treated with concentrated nitric acid (1 c.c.). On cooling and stirring the dark red solution an orange red crystalline solid separated out. The mixture was then diluted with ether and filtered; the solid residue was washed with ether and crystallised from chloroform. It formed orange red plates melting at 186–87°. Mixed melting point with the quinone prepared from 2-hydroxy-3 : 4 : 6-trimethoxy chalkone was not depressed.

Methylation of lawsone: 2-*methoxy-α-naphthoquinone* (*XXXI*)

2-Hydroxy-α-naphthoquinone was prepared from 1-amino-2-naphthol-4-sulphonic acid by the method of Fieser[12] and also by extracting the leaves of *Lawsonia alba*[14]. The two samples were identical in all respects.

A solution of 2-hydroxy-α-naphthoquinone (1 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (1 c.c., excess) and potassium carbonate (5 g.). The latter immediately assumed bright red colour due to the formation of a potassium salt. It was refluxed for 3 hours whereby most of the red colour of the solid was lost. Heating was stopped at this stage, the solid filtered and washed with hot acetone and the filtrate distilled. A pale yellow crystalline solid was left behind which was crystallised from benzene when it appeared as pale yellow narrow rectangular plates melting at 183–85°. Mixed melting point with a sample of 2-methoxy-α-naphthoquinone prepared by the method of Fieser, was not depressed. Yield, 0·9 g. It was insoluble in aqueous sodium bicarbonate but slowly dissolved in aqueous sodium hydroxide giving a yellow colour which changed to orange red. When this solution was acidified, 2-hydroxy-α-naphthoquinone was obtained.

Particular care should be taken in the above methylation to watch the course of the reaction and to stop it at the proper stage. Longer heating brings about further changes and the yield suffers. It is a disadvantage to use only one molecule of dimethyl sulphate. The reaction is then slow and due to the long heating dark coloured products are formed.

Methylation of benzoquinone

1*st method.*—A solution of benzoquinone (1 g.) in acetone (25 c.c.) was refluxed with dimethyl sulphate (1 c.c.) and potassium carbonate (5 g.) for 6 hours. The dark coloured reaction mixture was filtered, the solid washed with a little acetone and the filtrate distilled. The residue was extracted with

ether; on evaporating the ether extract a yellowish brown oil remained which crystallised on stirring. It melted at 58° alone or in admixture with an authentic sample of quinol dimethyl ether. Yield, 0·3 g.

2nd method.—Benzoquinone (1 g.) was dissolved in 5% aqueous sodium hydroxide (25 c.c.) and the dark green solution shaken with dimethyl sulphate (5 c.c.). A dark brown solid product separated out. The mixture was extracted with ether and the ether extract evaporated when a crystalline solid was obtained. It melted at 58° and was identical with quinol dimethyl ether. Yield, 0·2 g.

Benzoylation of benzoquinone

Benzoquinone (1 g.) was dissolved in 10% aqueous sodium hydroxide (50 c.c.) and the solution shaken with benzoyl chloride (5 c.c.) until it was all used up. The pale brown solid that separated out was filtered, washed and crystallised twice from benzene when colourless needles separated out melting at 200–02° identical with quinol dibenzoate. Yield, 0·5 g.

Action of alkali on Gossypetone tetramethyl ether (III)

The above flavoquinone was prepared from the hexamethyl ether of gossypetin using nitric acid as already described.[1]

Finely powdered gossypetone tetramethyl ether (0·3 g.) was made into a suspension with water (3 c.c.) and 10% aqueous sodium hydroxide (10 c.c.) added. The dark bluish violet solution was stirred for a minute and acidified with concentrated hydrochloric acid. The mixture was raised to the boil and the yellowish brown precipitate filtered, washed and crystallised from alcohol when it appeared as glistening golden yellow needles melting at 250–52°. It was identical with 5: 8-dihydroxy-3: 7: 3′: 4′-tetramethoxy flavone (V) prepared by the reduction of the above quinone with sulphur dioxide. Yield, 0·15 g.

Methylation of gossypetone (XXXII)

Gossypetone (0·2 g.) prepared according to the method of Perkin,[13] was dissolved in acetone (25 c.c.) and refluxed with dimethyl sulphate (1 c.c.) and potassium carbonate (5 g.). The solution first assumed a deep brown colour but it slowly became paler. After 8 hours the solvent was distilled off, water added and the solution extracted with ether. On concentrating the ether extract a small quantity of a white crystalline solid separated. It was filtered, washed with a little ether and recrystallised from alcohol when it separated out as colourless needles melting at 170–72° and identical with the hexamethyl ether of gossypetin (IV).

Methylation of gossypetone tetramethyl ether (III)

A solution of gossypetone tetramethyl ether (0·2 g.) in acetone (25 c.c.) was methylated with dimethyl sulphate (0·5 c.c.) and potassium carbonate (3 g.). After refluxing for 8 hours the product was worked up as in the previous case. It crystallised from alcohol as colourless needles melting at 170–72° and identical with the hexamethyl ether of gossypetin (IV).

Summary

Using typical examples, some of which are new, oxidative demethylation of methoxy benzenes, ketones, chalkones and flavones with nitric acid is discussed. The flavones without exception undergo simple conversion into para quinones. The others fall into two categories: (*a*) 1 : 2 : 4 : 5-Tetramethoxy benzene and its derivatives suffer only oxidative demethylation like the flavones to yield the corresponding para quinones. (*b*) 1 : 2 : 3 : 5-Tetramethoxy benzene and its derivatives, either ketones or chalkones, on the other hand undergo further change involving demethylation of another methoxyl group yielding hydroxy quinones. In the case of ketones and chalkones this second stage demethylation involves the methoxyl which is situated ortho to the ketonic carbonyl and which is subjected to the combined influence of this carbonyl and the one in the quinone group. These results are of importance in the study of pedicellin-pedicinin conversion.

Under favourable conditions hydroxy quinones can be methylated by means of dimethyl sulphate and potassium carbonate to the corresponding methyl ethers, *e.g.* lawsone. In some cases fully methylated ethers of the corresponding quinols could be obtained *e.g.* gossypetone. This is obviously due to the preliminary dismutation of the quinone into the corresponding quinol and complex products. The action of alkali on benzoquinone and tetramethyl gossypetone has been studied using different conditions.

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A NOTE ON THE CONSTITUTION OF GOSSYPITRIN

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In the study of the constitution of this glucoside there was originally difficulty in methylating it. It is very sensitive to alkali and undergoes decomposition. Diazo-methane effected only partial methylation,[1] the resistant 5-hydroxyl group being left out. However, methylation of the acetate using dimethyl sulphate and potash in aqueous acetone solution led to successful results.[2] The glucoside methyl ether was isolated and hydrolyssed and the product identified as 3 : 5 : 8 : 3′ : 4′-*O*-pentamethyl-gossypetin having a free hydroxyl in the 7-position, thus showing that gossypitrin is a 7-glucoside. Subsequently other methods of methylation have been examined in this laboratory. Methyl iodide and anhydrous potassium carbonate in dry acetone medium do not bring about complete methylation in the gossypetin series of flavonols.[3] On the other hand, the use of dimethyl sulphate has led to the desired results and the method is quite convenient and economical. Though gossypitrin is sparingly soluble in dry acetone, a fine suspension of it reacts with dimethyl sulphate and the fully methylated product is obtained in good yield.

In the earlier publication the melting point of the gossypitrin methyl ether was wrongly reported as 290°. The correct melting point is 177–78°. The same product is obtained by the methylation of the acetate as already described and by the direct methylation of the glucoside as now carried out. Originally the identification of the pentamethyl gossypetin was made by a comparison of its properties with the description given by Baker, Nodzu and Robinson[4] for their synthetic sample. It has now been possible to make this compound synthetically again for direct comparison and mixed melting point. Since in the study of partial methyl ethers of flavones and flavonols the ethyl ethers have been found to be useful derivatives, the 7-ethyl ether of *O*-pentamethyl gossypetin has also now been made and described.

Experimental

Methylation of Gossypitrin

Finely powdered gossypitrin (1·0 g.) was suspended in dry acetone (25 c.c.) and redistilled dimethyl sulphate (5 c.c.) and anhydrous potassium carbonate (6 g.) added. The mixture was refluxed for 30 hours on a water-bath, filtered and the inorganic salts washed with warm acetone. Distillation

of the solvent from the filtrate yielded a sticky red solid which crystallised from alcohol as almost colourless prisms; it slowly developed a yellow colour on exposure to air. It melted at 179–80°, did not dissolve in alkali and did not give any colour with alcoholic ferric chloride.

Methyl gossypitrin was also prepared by the method of Rao and Seshadri[2] and recrystallised from glacial acetic acid. It melted at 179–80° and did not depress the melting point of the sample described above.

Methyl gossypitrin was hydrolysed by boiling with 7% aqueous alcoholic (1 : 1) sulphuric acid for 2 hours. The product (pentamethyl gossypetin) crystallised from dilute alcohol as rectangular prisms melting at 250–1°. It was soluble in alkali and did not give any colour with ferric chloride. It was acetylated in the usual way with acetic anhydride and sodium acetate. The product crystallised from ethyl acetate as colourless prisms melting at 169–70°. It was insoluble in alkali and easily soluble in alcohol and ethyl acetate.

The pentamethyl gossypetin and its acetate were identical with synthetic samples of 3 : 5 : 8 : 3′ : 4′-pentamethoxy-7-hydroxy flavone and its acetate and the mixed melting points were undepressed. The ketone intermediate required for this synthesis was made by the symplified process recently reported.[5]

The pentamethyl gossypetin (0·2 g.) was ethylated by boiling with excess of ethyl iodide (0·5 c.c.) and ignited potassium carbonate (2 g.) in anhydrous acetone medium for 6 hours. The 7-ethyl ether crystallised from rectified spirit as pale yellow small prisms melting at 170°. It was insoluble in alkali and did not give any colour with ferric chloride. On reduction with magnesium and hydrochloric acid, a red colour was developed rapidly. (Found: C, 60·7; H, 5·9; loss on drying 3·8; $C_{22}H_{24}O_8$, H_2O requires C, 60·8; H, 6·0; H_2O, 4·1%.)

Summary

Gossypitrin is fully methylated by means of dimethyl sulphate and potassium carbonate in acetone medium. The pentamethyl gossypetin obtained by hydrolysis has been directly compared with a synthetic sample and mixed melting point taken. Its ethyl ether has also been made.

References

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2. Rao and Seshadri .. *Ibid.*, A, 1939, **9**, 177.
3. Rao, Reddy and Seshadri .. *Ibid.*, A, 1940, **12**, 495.
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SYNTHESIS AND STUDY OF 5: 6: 8-HYDROXY FLAVONOLS

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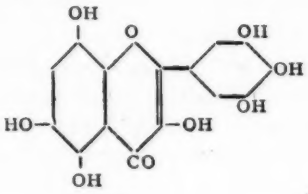
As already pointed out[1] nor-gardenin (I) is characterised by an extraordinary lack of colour effect in alkaline solutions and this forms an important contrast to the marked colour changes exhibited by the isomeric flavonols, hibiscetin and 6-hydroxymyricetin and even by the much simpler compound, robinetin (II).



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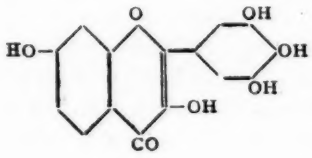
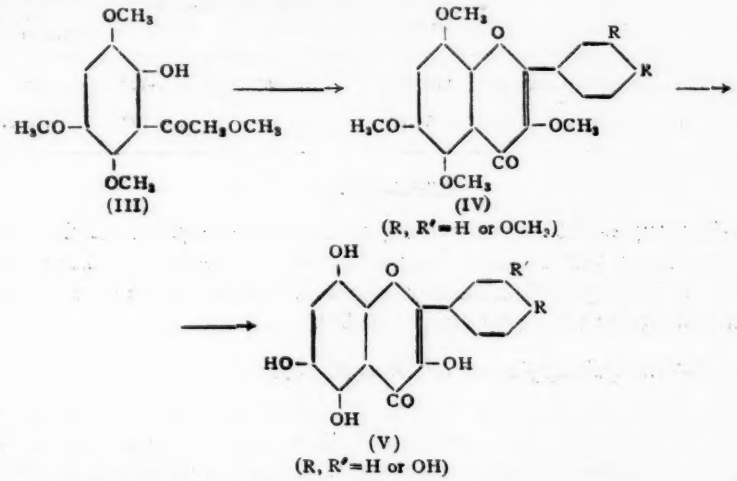


(II)

This was attributed mainly to the absence of the 7-hydroxyl group in nor-gardenin. It has therefore been felt necessary to prepare the analogues of nor-gardenin in order to have more examples. Further there is also the possibility of their being discovered in nature in future. Then the recorded properties of the synthetic compounds will render their identification more easy. Their total synthesis is very difficult. The only available method was used in the synthesis of 3: 5: 6: 8-tetramethoxy-flavone and this was described in an earlier publication.[1] The simpler alternative would require the synthesis of ω-3: 5: 6-tetramethoxy-2-hydroxy-acetophenone (III) and condensing it with the anhydrides and sodium salts of various acids. But no method has so far been developed for the synthesis of this ketone. However, it could be readily obtained by the alkali fission of methyl gardenin and the yield is quite high being about 50% of the weight of methyl gardenin taken. Hence this fission ketone has been employed for the condensation by the Allan-Robinson method. The synthesis using benzoic anhydride and sodium benzoate was described in the earlier paper.[1] The tetramethoxy compound (IV, R = R′ = H) was found to be identical with the one obtained from 3: 5: 6-trihydroxy flavone by nuclear oxidation. The two have now

been independently demethylated and the samples of the tetrahydroxy compound (V, R = R′ = H) thus produced compared. They are found to be identical in every respect. The synthesis has been further carried out using the anhydrides and sodium salts of anisic and veratric acids. Just as in the partial synthesis of gardenin and in the condensation using benzoic anhydride and sodium benzoate even in these two cases there is partial demethylation in the course of the reaction. But the crude products have been directly demethylated or methylated in order to obtain the penta- (V, R = OH, R′ = H) or hexa- (V, R = R′ = OH) hydroxy-compounds and their fully methylated derivatives (IV).



The melting points of the four flavonols of this series are embodied in the table given below. The following remarks could be made on the data: There is a gradual rise in the melting points of the hydroxy compounds with the increase in the number of hydroxyl groups whereas in the case of the methoxy compounds there is a maximum in the second member and then a decrease in the melting point as the number of methoxyls increases. The colour reactions are just the same for all the members of this group and the variation in the number of hydroxyl groups in the side phenyl nucleus seems to have absolutely no effect. These hydroxy compounds differ markedly from the isomeric 5: 6: 7-and 5: 7: 8-hydroxy flavonols. Thus there seems to be sufficient confirmation of the idea that the alkali colour reaction is very much dependent on the presence or absence of a hydroxyl group in this position. Another noteworthy feature is that Bargellini's test using sodium amalgam and alcohol is uniformly negative. The characteristic green flocks

given by the 5:6:7-hydroxy-flavones is not given. Even the small variation in the arrangement of the hydroxyl groups from 5:6:7- to 5:6:8-causes this difference. It has already been pointed out that even 5:6:7:8-hydroxyl compounds[2] do not respond to this test though there is only an addition of a hydroxyl group, the original 5:6:7-arrangement being kept up. There is therefore considerable amount of specificity in this reaction. With regard to the reduction using magnesium and hydrochloric acid in alcoholic solution the methyl ethers give considerably brighter colours than the corresponding hydroxy compounds.

	Tetra-hydroxy flavone	Penta-hydroxy flavone	Hexa-hydroxy flavone	Hepta-hydroxy flavone (norgardenin)
M.P. of the hydroxy compounds ..	218–20°	258–60°	275–77°	320°
M.P. of the methyl ethers ..	118–19°	142–44°	130–32°	116–17°

Experimental

2-Hydroxy-ω-3:5:6-tetramethoxy-acetophenone required for the following experiments was obtained by the fission of methyl gardenin using absolute alcoholic potash as already described.[1] It was in the form of bright yellow rectangular plates, melting at 88–89°.

3:5:6:8-*Tetrahydroxy-flavone* (*V*, $R = R' = H$)

The condensation of the ketone with benzoic anhydride and sodium benzoate has already been described.[1] The crude condensation product (0·5 g.) was dissolved in acetic anhydride (2 c.c.) and hydriodic acid (10 c.c.; d., 1·7) added with cooling under the tap. The mixture was gently boiled for one hour. After cooling, it was diluted with water and saturated with sulphur dioxide. The yellow solid that separated out was filtered and crystallised from acetic acid. It was obtained as bright yellow small prisms melting at 218–20°. (Found: C, 63·1; H, 3·8; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%.) The following reactions were carried out using an alcoholic solution of the substance. Ferric chloride gave first a green colour which changed to blue immediately followed by a greenish-blue precipitate. Magnesium and hydrochloric acid produced a red colour, *p*-benzoquinone a reddish-brown colour and sodium amalgam an immediate brown precipitate. The substance dissolved in aqueous sodium hydroxide, sodium carbonate and bicarbonate. In the first case a reddish-brown solution was first formed which changed to pale brown in the course of 5 minutes; in the second, a bright yellow solution was first produced which rapidly changed

to brown and in the last, there was first a greenish-yellow solution which changed to yellow.

Condensation of the ketone with anisic anhydride and sodium anisate

An intimate mixture of the ketone (1·0 g.) with anisic anhydride (10 g.) and sodium anisate (3 g.) was heated at 175–80° under reduced pressure for three hours. The product was dissolved in boiling alcohol (50 c.c.) and a 50% solution of potassium hydroxide (6 g.) was slowly added during 20 minutes while the solution was refluxing. The alcohol was removed under reduced pressure. The residue was dissolved in water and the aqueous solution was filtered. On saturating the aqueous filtrate with carbon dioxide a bright yellow solid separated out. It was extracted with ether. The ether solution when concentrated deposited bright yellow needles, giving an olive-green ferric chloride colour. Yield, 0·6 g.

3: 5 : 6 : 8 : 4′-*Pentahydroxy-flavone* (*V*, $R = OH$, $R' = H$)

The above condensation product (0·4 g.) was demethylated using hydriodic acid and acetic anhydride as already described for a similar case. The penta-hydroxy compound crystallised from acetic acid as bright yellow prisms melting at 258–60°. (Found: C, 59·3; H, 3·1; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%.) The colour reactions of this compound were just the same as those of the tetrahydroxy compound described earlier in this paper.

3: 5: 6: 8: 4′-*Pentamethoxy-flavone* (*IV*, $R = OCH_3$, $R' = H$)

The crude condensation product (0·2 g.) was dissolved in dry acetone (25 c.c.) and treated with dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (8 g.). The solution was refluxed for 30 hours and the potassium salts were filtered off. The acetone filtrate was concentrated and diluted with water when a colourless solid was obtained. It was filtered and crystallised from alcohol. It was thus obtained as colourless needles melting at 142–44°. (Found: C, 64·7; H, 5·1; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous alkali. With magnesium and hydrochloric acid it gave a deeper red colour than the corresponding hydroxy-compound.

Condensation of the ketone with veratric anhydride and sodium veratrate

This was carried out using the ketone (1·0 g.), veratric anhydride (10 g.) and sodium veratrate (5 g.) according to the procedure already described. The crude product was obtained as yellow needles which gave an olive green ferric chloride colour. Yield, 0·6 g.

3 : 5 : 6 : 8 : 3′ : 4′-Hexahydroxy-flavone (*V*, $R = R' = OH$)

The above condensation product (0·4 g.) was demethylated using hydriodic acid and acetic anhydride. The hexahydroxy-flavone crystallised from acetic acid as bright yellow prisms melting at 275–77°. (Found: C, 56·0; H, 3·5; $C_{15}H_{10}O_8$ requires C, 56·2; H, 3·2%.) The colour reactions of this compound also were the same as those of the compounds of this series already described.

3 : 5 : 6 : 8 : 3′ : 4′-Hexamethoxy-flavone (*IV*, $R = R' = OCH_3$)

The crude condensation product (0·2 g.) was methylated in dry acetone medium using anhydrous potassium carbonate and dimethyl sulphate, and following the procedure described already. The methyl ether crystallised from alcohol as colourless needles melting at 130–32°. (Found: C, 62·5; H, 5·2; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%.) It did not give any colour with alcoholic ferric chloride and was insoluble in aqueous sodium hydroxide. With magnesium and hydrochloric acid it gave a deeper red colour than the corresponding hydroxy compound.

Summary

In an earlier paper it was remarked that the colour reactions of nor-gardenin were rather extraordinary. Other flavonols belonging to the 5 : 6 : 8-hydroxy series and their methyl ethers have now been prepared using the fission ketone from methyl gardenin, and their properties studied. Their colour reactions resemble those of nor-gardenin and methyl gardenin closely. In general the hydroxy-flavonols of this series exhibit reactions with alkaline buffer solutions differing markedly from their isomers belonging to the 5 : 7 : 8- or 5 : 6 : 7- series thus emphasising the importance of the 7-hydroxyl for this purpose.

References

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2. Seshadri and Venkateswarlu .. *Ibid.*, 1946, **23**, 192.

SULPHANILAMIDES

Part I. Salts with Sulphonic Acids

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Certain aspects of the work carried out in this laboratory on the structural characteristics of organic compounds which lead to surface activity in relation to their use in textile processing[1] suggested an extension of these investigations in the field of chemotherapy. The adsorption of wetting agents and detergents by textile fibres indicates that a combination of surface-active compounds with drugs would probably lead to more active chemotherapeuticals, since affinity of a substance for bacteria has been considered as a requisite for its chemotherapeutic activity. The bactericidal and lytic action of a number of surface-active agents,[2] the potentiation of drugs by synergistic action with detergents,[3] and the activity of drugs modified in their chemical constitution by the introduction of structural features which lead to surface activity[4] have been studied in recent years.

The arylamine salts of aromatic sulphonic acids are useful in the characterisation of both the amines and the sulphonic acids,[5] and the object of the present work is to synthesise surface-active compounds from wetting agents containing sodium sulphonate groups and different sulphanilamides. Arylamine salts of sulphonic acids are relatively stable to mineral acids, but they break down on treatment with alkali and can in fact be estimated by titration with caustic soda solution. By virtue of their stability to mineral acids, the sulphanilamide salts should pass through the stomach, and under the alkaline condition in the intenstines liberate the drug component. Such an action would probably make these salts active intestinal bacteriostatic agents. The surface-active component should also lead to advantages due to the spreading, penetration, and emulsification properties associated with it.

Sulphanilamide salts of several aliphatic carboxylic acids, and aromatic, sulphonic and carboxylic acids have been mentioned[6-10] but do not appear to have been isolated in pure form and characterised. The bacteriostatic activity of some of the salts has been stated to be better than sulphanilamide, although the salts contained only 40 to 50 per cent. of the sulpha component.

Before attempting the synthesis of salts from surface-active agents, a preliminary study of salts prepared from naphthalene-2-sulphonic acid and

a series of sulphanilamides was undertaken. The salts were prepared by adding a boiling aqueous solution of the sodium salt of the sulphonic acid (one mole) to a hot solution of the sulphanilamide (one mole) in water containing hydrochloric acid (1·4 moles), and boiling the contents for about two minutes. The salts generally separated quickly on cooling, although in some cases it was necessary to leave the mixture overnight or even longer or to concentrate it to smaller bulk.

The salts of sulphanilamide and sulphathiazole were easily prepared, but salt formation in the case of sulphanilamides with basic N^1-substituents such as sulphapyridine, sulphadiazine and sulphaguanidine proved to be difficult in the early experiments in which the equivalent quantity of hydrochloric acid was used. In order to find out whether the basic N^1-substituents were in any way responsible for the failure of the N^4-amino groups to form ammonium salts, a series of salts of naphthalene-2-sulphonic acid with 2-aminothiazole, 2-aminopyrimidine, and 2-amino-4: 6-dimethylpyrimidine were prepared. In the preparation of these salts, it was found that addition of excess of hydrochloric acid was necessary for salt formation. Using excess of hydrochloric acid (up to 4 moles) naphthalene sulphonic acid salts of sulphapyridine, sulphadiazine, sulphamerazine, sulphaguanidine, N^1-acetylsulphanilamide, and *p*-aminobenzoic acid were readily prepared. Crystallisation of most of these salts was effected from dilute hydrochloric acid. To get a more soluble product the salt of sulphanilamide with phenol-*p*-sulphonic acid was prepared, and was found to melt at 241–42° (decomp.) as against 216–220° (decomp.) recorded in literature.[7] A mixture of the authentic salt and sulphanilamide hydrochloride gave the m.p. 216–20° (decomp.), showing that the compound described earlier was probably such a mixture.

The purity of the salts was estimated by titration with standard sodium hydroxide, in addition to elementary analysis. Sulphanilamide was not acidic to phenolphthalein, and its salt with naphthalene-2-sulphonic acid required one equivalent of sodium hydroxide corresponding to the ammonium salt linkage. Sulphathiazole was acidic to phenolphthalein and not acidic to methyl red. Its salt with naphthalene-2-sulphonic acid, when titrated against standard alkali using methyl red, therefore, required one equivalent of alkali corresponding exclusively to the salt linkage; using phenolphthalein the salt titrated for two equivalents of alkali corresponding to both the ammonium salt and the sulphonamido groups. The purity of the salts from other sulphanilamides were not determined by titration as they could not be obtained entirely free from traces of hydrochloric acid.

The formation of salts of arylamines with wetting agents containing a sodium sulphonate or a sulphate group has been applied for the estimation of fatty alcohol sulphates and the sulphonates.[11] Judging from the ease with which aromatic sulphonic acids such as phenol-*p*-sulphonic and naphthalene-2-sulphonic acid gave salts with the different sulphanilamides, one of the first wetting agents which was used for salt formation with sulphanilamide was dibutylnaphthalene sodium sulphonate (Nekal BX, I. G. Farbenindustrie). While most of the alkali salt merely decomposed to the free alkylnaphthalenesulphonic acid under the acid conditions of the reaction, a small quantity of the desired ammonium salt could be isolated and characterised. Sodium dioctylsulphosuccinate (Aerosol OT, American Cyanamid Co.) gave a light brown hydroscopic salt with sulphanilamide. It could not be crystallised, but the analysis and the properties of the substance gave definite indication of ammonium salt formation. 4-Laurylamidotoluene-2-sodium sulphonate,[12] which is a powerful wetting agent, gave a hydroscopic amorphous light brown salt with sulphanilamide possessing very good wetting power, and this compound was obtainable in analytically pure condition.

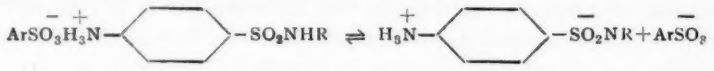
With the object of determining the relative ease with which *p*-aminobenzoic acid (an essential growth factor for the bacteria-enzyme system) and sulphanilamide combine with organic anions such as the sulphonic ion, the salt of sulphanilamide and naphthalene-2-sulphonic acid was treated with *p*-aminobenzoic acid under various conditions. While *p*-aminobenzoic acid replaces sulphanilamide appreciably at elevated temperature (about 100°) to give the salt of the former with the sulphonic acid, replacement could be noticed to a small extent even at room temperature.

Bacteriostatic Activity of the Ammonium Salts

The *in vitro* tests indicated that the salts are more active than the parent sulphanilamide in spite of the lower content (45–56%) of the active sulpha components. Sulphanilamides or naphthalene-2-sodium sulphonate when tested separately in the amounts present in the salts are inactive. The enhanced potency of the salts cannot be due to increased solubility as mentioned by Smyth and Carpenter,[6] because the salts are less soluble as compared to the sulpha components.

Since Woods and Fildes[13] first suggested that *p*-aminobenzoic acid is an essential metabolite necessary for bacterial growth and that the bacteriostatic action of sulphanilamides is due to their ability to block the enzyme system or systems in competition with *p*-aminobenzoic acid, various hypotheses[14–16] based on this generalisation have been advanced as regards the mode of action and the varying potency of different sulphanilamides. The

increased activity of the ammonium salts now prepared suggests that in sulphanilamides and *p*-aminobenzoic acid both the acidic and basic parts of the molecule are involved in the bacteriostatic activity. A sulphanilamide should then have maximum activity if the basic and acidic ends of the molecule are rendered more reactive by ionisation leading to a zwitterionic structure. The potentiation of sulphoanilamides by ammonium salt formation could therefore be due to the fact that by ionisation the sulpha components would acquire the more reactive zwitterion form (I).



(I)

Klotz and Gruen[17] have shown that zwitterion formation in sulphanilamide is negligible, but *p*-aminobenzoic acid is present as zwitterions to the extent of 3 per cent. at pH 7. Bell and Roblin[14] obtained indirect evidence to suggest that the ionised carboxyl group in *p*-aminobenzoic acid increased the basicity of the amino group threefold. Recently, Fuller[18] has suggested that the activity of sulphanilamides is determined both by the acidic sulphonamide group and the basic amino group.

The acidic and the basic ends of the sulphanilamide molecules probably enter into complex formation with the basic and acidic active centres of the bacterial enzyme, either separately or at the same time, since the latter is amphoteric in character and contains both positively and negatively charged groups between the extreme limits of pH 2–13 like many other proteins.[19]

In the light of the relation between metabolites and their structurally related antagonists,[20] the formation of complexes by sulpha drugs (antagonists) in competition with complex-formation by *p*-aminobenzoic acid (essential metabolite) will depend on the relative strength of the electrical charges on *p*-aminobenzoic acid and the sulpha drugs, as also on the charges at the points of attachment in the enzyme.

When the ammonium salt ionises ultimately to (I), the zwitterionic character of the latter will be further stabilised by complementary inductive effects of the positively charged ammonium and negatively charged sulphonamide groups. The increased activity of the ammonium salts could be explained on the basis of increased attraction between the active centres in the enzyme and the zwitterions (I) of the sulphanilamide salts, as compared to the parent sulphanilamides, the increased attraction being due to the increased electrical charges on the amino and the sulphonamido groups in the form (I). Under optimum conditions these attractive forces may be comparable in strength to the attractive forces between the essential meta-

bolite, *p*-aminobenzoic acid, and the active centres in the enzyme system. As mentioned earlier, it has been found that the replacement of sulphanilamide from its salts with naphthalene-2-sulphonic acid takes place to some extent even at room temperature. The sulphonic anion might therefore make a small contribution to the bacteriostasis by removing part of the essential metabolite, *p*-aminobenzoic acid, by salt formation, as also by complex formation with the positively charged parts of the enzyme molecule. Inactivation of sulpha drugs *in vivo* during metabolism by N^4-acetylation might perhaps be prevented or minimized by the use of the sulphanilamide salts instead of the parent sulpha componets.

The variation in the activity of different N^1-substituted sulphanilamides could be explained on the basis of the difference in the contribution of the zwitterionic form due to variation in the acidity of sulphonamido groups depending on the N^1-substituent.[14] The greater the acidity of the sulphonamido group, the greater will be its inductive effect on the positive charge of the N^4-ammonium group. It is in fact conceivable that with high acidity of the sulphonamido group, its ionisation might precede the formation of (I). The effect of changes in pH on the activity of the sulphanilamides and on the antagonising power of *p*-aminobenzoic acid (*cf.*, Fuller[15]) could also be explained similarly.

Compounds derived by N^1-substitution of sulphanilamides include most of the therapeutically important sulpha drugs, susbtitution in other positions generally leading to inactive products. The sulphonamide salts now prepared are more active than the parent sulpha drug in spite of the modification of the N^4-amino group. The physiological properties of the sulphanilamides, such as absorption-excretion characteristics, toxicity and easy accessibility to the site of infection, could also be modified by varying the nature of the sulphonic anion in the salts.

Experimental

General Method

Sulphanilamide salt of naphthalene-2-sulphonic acid.—A hot aqueous solution naphthalene-2-sodium sulphonate (4·6 g. in 100 c.c.) was added to a hot solution of sulphanilamide (3·44 g.) in water (20 c.c.) and concentrated hydrochloric acid (2·5 c.c.). After boiling for about 2 minutes and decolourising (norit), the solution was cooled gradually to room temperature when lustrous white flakes of the salt separated, m.p. 262–63° C. (5·0 g.); raised to 263–64° C. on further recrystallisation from hot water (Found: N, 7·3; S, 17·2. $C_{16}H_{16}O_5N_2S_2$ requires N, 7·4; S, 16·8%. 0·200 g. required 5·3 c.c. of 0·1 N sodium hydroxide. Calc.: 5·2 c.c.).

Sulphathiazole salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (4·6 g.) sulphathiazole (5·1 g.), concentrated hydrochloric acid (2·5 c.c.), and water (250 c.c.) gave the salt (8·0 g.) which, crystallised in white needles from water, m.p. 214–15° C. [Found: N, 9·2; S, 20·5. $C_{19}H_{17}O_5S_3N_3$ requires N, 9·1; S, 20·7%. 0·200 g. required 4·2 c.c. (methyl red) and 8·6 c.c. (Alkali Blue 6B) of 0·1 N sodium hydroxide. Calc., 4·3 c.c. and 8·6 c.c. respectively.]

2-*Aminothiazole salt of naphthalene-2-sulphonic acid.*—Naphthalene-2-sodium sulphonate (0·92 g.), 2-aminothiazole (0·4 g.), 1·5 N hydrochloric acid (5·27 c.c.), and water (5·0 c.c.) gave the salt (0·68 g.) which after two crystallisations from water gave colourless hexagonal tablets, m.p. 162–64° (Found: N, 8·9. $C_{13}H_{12}O_3N_2S_2$ requires N. 9·1%).

2-*Aminopyrimidine salt of naphthalene-2-sulphonic acid.*—The salt was prepared as above from 2-aminopyrimidine (0·37 g.). The reaction mixture after leaving overnight and concentration gave the salt (0·625 g.) which after three recrystallisations from water separated as colourless short needles, m.p. 190–192° C.; mixed with 2-aminopyrimidine hydrochloride (m.p. 196° C.) it gave m.p. 160–170° (Found: N, 13·2; S, 10·1. $C_{14}H_{13}O_3N_3S$ requires N, 13·9; S, 10·5%).

2-*Amino*-4: 6-*dimethylpyrimidine salt of naphthalene-2-sulphonic acid.*—Naphthalene-2-sodium sulphonate (4·6 g.), 2-amino-4: 6-dimethylpyrimidine (2·46 g.), concentrated hydrochloric acid (5·0 c.c.), and water (40 c.c.) after boiling, concentration and cooling gave the salt as white needles, m.p. 107–10° C. (8·5 g.); raised to 155–56° after drying in vacuum at 100°. After two recrystallisations from water the anhydrous salt melted at 159–60° C. (Found: N, 11·7; S, 9·4. $C_{16}H_{17}O_3N_3S$ requires N, 12·6, S, 9·6%).

Sulphapyridine salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (2·3 g.), sulphapyridine (2·48 g.), concentrated hydrochloric acid (2 c.c.), and water (30 c.c.) gave the salt partly as an oil and partly as a crystalline solid on cooling. The oil solidified on cooling in a freezing mixture and the combined solid (2·8 g.) was crystallised from alcohol when the salt separated as lustrous colourless needles; dried at room temperature for 3 hours at 5 m.m., m.p. 70–75° C. (Found: N, 8·34. $C_{21}H_{19}O_5N_3S_2$, C_2H_6O requires N, 8·35%). The salt after drying at 100° C. under reduced pressure gave a cream coloured powder, m.p. 152–53° (Found: N, 9·6. $C_{21}H_{19}O_5N_3S_2$ requires N, 9·2%).

Sulphadiazine salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (2·3 g.), sulphadiazine (2·5 g.), concentrated hydrochloric acid (4·0 c.c.), and water (55 c.c.) after boiling and cooling to 30-

35° C. gave the salt as lemon yellow needles, m.p. 188–89° (3·72 g.). The mother liquor on cooling in ice gave a further quantity of the salt as lustrous cream coloured short needles, m.p. 188° (0·55 g.) (Found: N, 11·9; S, 13·6. $C_{20}H_{18}O_5N_4S_2$ requires N, 12·2; S, 14·0%). The salt readily dissociated in water and recrystallisation could only be effected from acidulated water.

Sulphamerazine salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (4·6 g.), sulphamerazine (5·28 g.) concentrated hydrochloric acid (5 c.c.), and water (50 c.c.) gave the salt as cream coloured needles, m.p. 117–20° (9·5 g.); raised to 118–20° on further recrystallisation from acidulated water (Found: S, 13·0; $C_{21}H_{20}O_4N_4S$ requires S, 13·5%).

Sulphaguanidine salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (2·3 g.), sulphaguanidine (2·14 g.), concentrated hydrochloric acid (1 c.c.), and water (35 c.c.) were boiled together and left overnight and the salt which separated as colourless flat needles (3·4 g.) was recrystallised from acidulated water. After drying at 120–30°/150 m.m. it softens at 186° and melts at 225–26° (Found: N, 13·1; S, 15·8. $C_{17}H_{28}O_5N_4S_2$ requires N, 13·3; S, 15·2%).

N^1-Acetylsulphanilamide salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (2·3 g.), N^1-acetylsulphanilamide (2·14 g.), con-concentrated hydrochloric acid (1 c.c.), and water (30 c.c.) after boiling and cooling gave lustrous flakes of the salt, m.p. 250–55° C. (1·65 g.); raised to 253–54° after recrystallisation from acidulated water (Found: N, 7·0; S, 15·5. $C_{18}H_{18}O_6N_2S_2$ requires N, 6·3; S, 15·1%).

p-Aminobenzoic acid salt of naphthalene-2-sulphonic acid.—Naphthalene-2-sodium sulphonate (1·15 g.), *p*-aminobenzoic acid (0·7 g.), concentrated hydrochloric acid (0·5 c.c.), and water (15 c.c.) gave lustrous flakes of the salt; soften at 252°, m.p. above 260° (decomp.) (Found: N, 3·9. $C_{17}H_{15}O_5$ NS requires N, 4·1%).

Sulphanilamide salt of phenol-p-sulphonic acid.—The sulphonic acid (8·7 g.) was dissolved in dilute aqueous sodium hydroxide (2·1 g. in 50 c.c.) and the solution was boiled with sulphanilamide (8·6 g.), concentrated hydrochloric acid (7·0 c.c.), and water (70 c.c.). White needles of the salt separated on cooling, m.p. 240–41° (11·0 g.); raised to 241–42° on further recrystallisation from acidulated water (Found N, 8·3. $C_{12}H_{14}O_6N_2S_2$ requires N, 8·1%.)

Sulphanilamide salt of Nekal BX.—Nekal BX (9·42 g.), sulphanilamide (5·16 g.), concentrated hydrochloric acid (3·65 c.c.), and water (100 c.c.) were boiled together and the solution was cooled in ice when a heavy oil

separated. The clear supernatent liquid was decanted and concentrated, and after cooling for a week in the refrigerator gave white flakes of the salt, m.p. 195–200° C. (3·0 g.). After recrystallisation from acidulated water it gave m.p. 220–222° (Found: N, 5·9. $C_{24}H_{35}O_3N_2S_2$ requires N, 5·7%). The heavy oil from the crude reaction mixture analysed for dibutylnaphthalene sulphonic acid.

Sulphanilamide salt of Aerosol OT.—Aerosol OT (13·2 g.), sulphanilamide (5·15 g.), 1·5 N hydrochloric acid (60 c.c.), and water (150 c.c.) were boiled together and the mixture evaporated to dryness and the residue was extracted in a soxhlet with absolute alcohol. The alcoholic extract gave a cream coloured viscous solid after removal of the solvent analysis of which indicates the formation of the salt.

Sulphanilamide salt of 4-laurylamidotoluene-2-sodium sulphonate.—The wetting agent (5·9 g.), sulphanilamide (2·5 g.), concentrated hydrochloric acid (1·65 c.c.) and water (120 c.c.) were boiled together and cooled when a thick jelly was obtained. It was evaporated to dryness and the residue was extracted with absolute alcohol in a soxhlet and the alcoholic solution on evaporation gave the salt as a light brown hydroscopic powder (Found: N, 8·1; S, 11·2. $C_{25}H_{39}O_6N_3S_2$ requires N, 7·7; S, 11·8%).

Replacement of sulphanilamide from its salt with naphthalene-2-sulphonic acid by p-*aminobenzoic acid*: *Method A.*—The sulphanilamide salt (0·38 g.), *p*-aminobenzoic acid (0·137 g.), and water (20 c.c.) were boiled under reflux for one hour. The solution was cooled in ice when lustrous flakes separated (0·045 g.) which after recrystallisation gave m.p. above 260° (decomp.) undepressed when mixed with the salt of *p*-aminobenzoic acid with naphthalene-2-sulphonic acid.

Method B.—A solution of the sulphanilamide salt (0·38 g.) and *p*-aminobenzoic acid (0·137 g.) in water (60 c.c.) was left at room temperature (26-29° C.) for 10 days. The light brown solid obtained by evaporation at room temperature was stirred with water (16 c.c.) and filtered. The residue (0·105 g.) after recrystallisation was found to be the unreacted sulphanilamide salt. The mother liquor was clarified (norit), concentrated and cooled when pale brown needles, m.p. 175–85° (decomp.) were obtained; raised to m.p. above 260 (decomp.) by recrystallisation from water, and undepressed when mixed with the salt of *p*-aminobenzoic acid.

Method C.—A solution of the sulphanilamide salt (0·38 g.) and *p*-aminobenzoic acid (0·137 g.) in 1 per cent. sodium hydroxide (16 c.c.) was acidified with concentrated hydrochloric acid (0·5 c.c.). Small rods separated, m.p. 260–67° (0·175 g.), which were identical with the unreacted

sulphanilamide salt. The filtrate was cooled in ice when lustrous colourless flakes separated, m.p. above 260° (decomp.), undepressed when mixed with the salt of *p*-aminobenzoic acid. The experiment indicates the competitive reactivity of *p*-aminobenzoic acid and sulphanilamide for organic anions such as naphthalene-2-sulphonic in forming ammonium salts.

Bacteriostatic activity of the salts.—The sulphonamides and their salts were tested for bacteriostatic activity, *in vitro* against *E. coli* and *Staphylococcus aureus*, using the following media: (1) 1 per cent. casein hydrolysate, (2) Muir's synthetic medium[21] containing 1 per cent. casein hydrolysate, and (3) beef extract (0·4%) (Lab-Lemco, Oxo-Ltd., London), peptone (1%) and sodium chloride (0·5%).

The tests were carried out at pH 7·6 at 37° and the growth of the bacteria was followed visually by the appearance of turbidity. The concentration of the drug in milligrams per cent. required to prevent the growth after 72 hours was determined. When Muir's synthetic medium alone was used no growth was observed for *Staphylcoccus aureus*. Satisfactory results were, however, obtained when the medium (2) was used. The results of the tests on the salts of sulphonamides with naphthalene-2-sulphonic acid using the three media are given in the following table:

Sulpha drug	Per cent. sulpha drug in the salt	Medium	Minimum effective concentration mg.%			
			Staph. aureus		*E. coli*	
			Salt	Parent drug	Salt	Parent drug
Sulphanilamide ..	45·3	1	500	500	500	500
		2	400	600	500	500
		3	1050	1050	500	800
Sulphathiazole ..	55·1	1	8	12	8	10
		2	8	10	8	12
		3	300	400	400	500
Sulphapyridine ..	54·4	1	12	22	14	22
		2	14	22	12	22
Sulphadiazine ..	54·3	1	8	20	10	22
		2	12	20	10	22
Sulphamerazine ..	56·1	1	20	40	30	30
		2	20	40	30	30
Sulphaguanidine ..	50·7	1	250–300	250	250	300
		2	250	250–300	250	250–300
N^1-Acetylsulphanilamide ..	50·7	1	150	200	150	225
		2	150	200	175	225
		3	400	500	500	500

The results for the bacteriostatic activity of sulphonamides using inhibitor-free media 1 and 2 were comparable with those obtained by other workers.[14] The salts proved to be more active than their sulpha components although they contained only 45–56 per cent. of the sulpha drug. When medium (3) was employed considerable quantities of the sulpha drugs and their salts were required and the inhibitory confentration for sulphapyridine, sulphadiazine, sulphamerazine and sulphaguanidine and for their respective salts could not be determined due to lack of solubility. In medium (3) the salts showed nearly equal bacteriostatic activity in spite of the divergent activity of the sulpha components. The tests on the salts derived from wetting agents could not be carried out due to insufficient quantity of the analytically pure materials.

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MONAZITE IN THE BEACH SANDS OF VIZAGAPATAM DISTRICT

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Introduction

The study of the beach sands of the eastern coast is a neglected aspect of Indian Geology. In view of the potential economic importance of this subject and its academic value, a study of the beach sands of Vizagapatam, Waltair and environs from Rushikonda in the north to Yarada village in the south has been taken up by us. In recent years, monazite has attained both strategic and industrial importance and the potentialities of this mineral in India require to be carefully scrutinized. The only reference to this subject is in a publication, by Tipper (1914) where he casually mentions the reported occurrence of the mineral on the coast at Waltair and Bhimilipatam by Kemp and Cross respectively. Occurrence of monazite in all the samples now investigated by the authors is a most significant result and this paper deals mainly with that aspect of the problem.

Description of the Vizagapatam Beach

The Vizagapatam beach which runs roughly N.E.-S.W. having a width of 50′ to 300′ is situated between latitudes 17° 39′ and 70° 45′ and longitudes 83° 16′ 50″ and 83° 21′ 30″. The coastal area presents a hilly and rugged topography, with numerous bad lands and sand dunes. The important hills that form conspicuous landmarks in this area are the Simhachalem range to the north and Yarada hills to the south. These hills are composed mainly of khondalites and leptynites, into which are intruded pegmatites, charnockites and granites. It may be mentioned that the geology of the Vizagapatam district bears a close resemblance to that of Travancore (Tipper, 1914, *loc. cit.*, p. 186) where monazite sands occur in profusion as beach concentrates along with ilmenite, sillimanite, garnet, zircon, etc. These geological formations, on disintegration and decomposition, contribute the loose talus material to the red loams of Waltair highlands and in part to the beach sands. A tidal basin spreads out to the west of the town through a connecting channel fringing the northern slope of the Yarada hill. The channel forms the present harbour. A good part of the salty

marsh of this tidal basin is reclaimed. The bad lands of Waltair are cut by many rivulets from the hills which fall into the Bay of Bengal. Chief among them are the Ootagedda stream between Waltair and Vizagapatam and Hanumanthavaka gedda to the north of Waltair and they transport the major part of the detrital sediment from the hills to the sea during the rainy season. The ill sorted red loam thus carried by the rivulets to the sea is thoroughly washed free of the clay material by the waves and carried to the deeper parts of the sea. Coarser particles like quartz, and other heavy minerals are deposited as sand along the beach, where through wave action they are further sorted according to their specific gravities and sizes. The black sands containing heavy minerals are found concentrated in patches by wave action over the predominantly quartz sands of the beach. It is also known from the investigations of the Vizagapatam harbour authorities that the currents bring up, from south to north, vast quantities of sands. Thus the beach sands not only represent the detrital material brought from interior by the streams but also those pushed up gradually from the southern coastal areas by currents. It is apparent from this fact that the whole of the coastal area which is fringed by Eastern Ghats consisting mainly of khondalites and charnockites deserves a most careful investigation.

Experimental Work

The black sands as well as white sands were sampled at suitable intervals along the beach. Out of these, six type samples, three black sand concentrates and three white sands, were taken for the present investigation wherein sedimentary petrographic methods have been adopted. They were cleaned of the ferruginous and calcareous coating by acid treatment and repeated washings. They were then dried and subjected to mechanical analysis. They were sieved by I.M.M. sieves of 10, 30, 60, 90, 120 and 150 meshes. All the fractions except the positive fractions of 10, 30 and 60 meshes (which contain little or no heavy minerals) were subjected to heavy mineral separation in Thoulet solution. The heavy crops thus obtained from various mechanical fractions were separated electromagnetically into strongly magnetic and feebly magnetic fractions. The weights of the fractional products were determined at each stage. They were carefully sampled and mounted on slides for optical study and the percentages of occurrence of various minerals were determined with the help of the mechanical stage.

Results

Results for a typical sample of black sand concentrate, are given below:

Sample taken : 1000 gms.

Minerals identified	+ 60 mesh and above (740 gm.)	−60 to −150 mesh (260 gm.)		
		Heavy minerals 252 gm.		Light Minerals 8 gm.
		Quantity	Percentage	
		gms.		
Monazite ..	Trace	20	8	
Magnetite .	bulk	203	80	
Garnet ..	Small amount	10	4	Mostly silica and felspars
Ilmenite ..	do	15	6	
Zircon ..	Trace	2	1	
Sillimanite ..	Small amount	2	1	
Quartz and Felspar ..	The rest	..	..	

Several other samples containing larger percentages of monazite have been analysed and fuller details with comprehensive data will be published in a later communication.

From the above study the minerals recognised in the sands are quartz, felspar, garnet, sillimanite, ilmenite, magnetite, monazite, zircon, rutile, hypersthene, tourmaline and micas. Attention may be drawn to the similarity of the mineral assemblage of this area to that of Travancore beach sands (P. Viswanadhan, 1946). It was found that the mineral species have definite preferential distribution in size in various fractions. Rock fragments are restricted to + 10 mesh fraction; admixture of rock fragments, quartz and felspar, to + 30 mesh fraction; quartz and felspar, to + 60 mesh fraction; garnet and sillimanite to + 90 mesh fraction; and monazite and zircon, to + 120 and + 150 mesh fractions. Magnetite, hypersthene, and ilmenite are found in all the fractions. In general it is found that the samples which have less amount of heavy minerals (white sands) show increasing concentrations of these with decreasing size of the sieve whereas the black sands show decreasing concentration of heavy minerals with the decreasing size of the sieve. The monazite is far more preponderant in the black sand concentrates than in the white sands.

The percentage of mineral assemblage shows a fairly wide variation in different samples but in general, magnetite is most abundant, followed by monazite, garnet, sillimanite, zircon, ilmenite, hypersthene, etc.

Among the minerals, zircon shows well developed prism and pyramid faces, sillimanites are in laths, tourmalines are prismatic, and monazite is well rounded. Monazite grains contain inclusions of which zircon is easily identified. The black sand concentrates contain monazite to about 2% of the bulk and 8% of the − 60 mesh and this is an important result.

Detailed investigations are under progress with regard to quantitative estimation of the various mineral assemblages from a larger number of samples as also the chemical composition of monazite and other heavy minerals.

Summary and Conclusion

The beach sands of the Vizagapatam coast between Yarada village and Rushikonda, covering a distance of about ten miles have been taken up for detailed study by sedimentary petrographic methods. Six representative samples from the collection, three of white sands and three of black sands, were subjected to mechanical, heavy mineral, and magnetic separation and the products thus obtained gravimetrically and optically estimated. It is found that of the heavy mineral suite, magnetites are most abundant, followed by monazite, garnet, sillimanite, zircon and ilmenite. At least about 2% of the black sand concentrate consists of monazite. Excluding + 60 mesh material, monazite is found to be 8% of the bulk of black sands. Though the white sands invariably yield monazite, their quantity is proportionately insignificant. Further investigations are in progress.

In conclusion, the authors are grateful to Prof. S. Bhagavantam for his interest in this work, valuable suggestions and for affording facilities in his laboratories for the electromagnetic separation.

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SOME OBSERVATIONS ON THE CHEMISTRY OF GLYCERIDES—PART I

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The investigation of the glyceride composition of a large number of fats by the more modern methods led Professor Hilditch[1] to suggest the rule of even distribution. The depot fats of the mammalia and various other land animals, a group of vegetable fats containing large proportions of C_{14} and lower saturated acids and the mammalian milk fats fall outside the scope of this rule. An attempt[2] has been made to explain this divergence on the basis of bio-hydrogenation followed by selective absorption to give depot fats; and a different mechanism to give mammalian milk fats.[3] Smith and Dastur[4] found a decrease of about 90% in the lower fatty acids of milk with an equivalent increase of oleic acid during fasting of cows. The finding was interpreted to indicate that the lower fatty acids represent intermediate products in the synthesis of oleic acid (see reference 24 for a similar idea). So far no attempt seems to have been made to account for the divergence in the group of vegetable fats.

Fractional crystallisation studies showed that the proportion of fully saturated glycerides in fats from different sources differ widely even when they have the same saturated-unsaturated acid ratio. Cacao butter,[5] *Garcina indica* fat[9] Borneo tallow[7] were found to contain not more than traces of fully saturated glycerides; whereas beef and mutton tallows[8] of similar saturated acid content and a Laurel kernal fat[9] of the same saturated-unsaturated acid ratio were found to contain 16% and 30% respectively of saturated glycerides. Further, Bailey[10] has shown that even those animal fats which contain fully saturated glycerides in proportions close to those required by chance distributions and which Longenecker[11] has suggested might probably be containing the other glyceride types also in proportions required by chance distribution, do not seem to fit into any established order. On interesterification of such fats,[12] fats differing greatly from the originals as regards physical properties resulted.

The synthesis of body fats and their transport by blood is also important in this connection. Parry and Smith[13] made the interesting observation that ox blood contains a high proportion of C_{20} and C_{22} unsaturated acids.

These acids must have a bio-synthetic origin as they are absent in the usual foodstuffs and consequently absent from the depot fats of the animals. Esterification of polyhydric alcohols[14] with mixtures of saturated and unsaturated acids produce fats with chance distribution of glyceride types. Since fats perform a number of vital functions[15] the formation of natural fats *in vivo* requires further study.

The GS_3 content in various natural fats are known with a reasonable degree of accuracy and in this contribution we are recording certain interesting conclusions regarding them. We have made use of published data[16] regarding GS_3-content and for other glyceride groups (forthcoming publication) we shall be drawing on our own results. Hilditch and Jones[17] pointed out an increase in the molar proportion of GS_3 corresponding to an increase in the proportion of saturated to unsaturated acids and that GS_3 varies as the cube of the molar percentage of saturated acids. It has also been pointed out[18, 19] that animal fats rich in stearic acid appear to be similar in GS_3-content and the mammalian milk fats resemble stearic rich animal fats as far as their GS_3 content is concerned. Whole tallows show GS_3-content higher than S^3, oleo-oils show consistently lower values, Bababssn fat[20] shows approximate identity; and so far as we know these constitute all the published references to the subject and is clearly limited to statements of approximate similarity of GS_3 to S^3 in certain groups of natural fats.

The relationship existing between GS_3 and S^3 may be expressed either as $GS_3 = K \times S^3$ or $S^3 \pm K$, where K is a constant. In the former case GS_3/S^3 remains a constant and in the latter $GS_3 - S^3$ is a constant. The mechanism involving the addition or elimination of a fixed quantity of fully saturated glycerides, irrespective of the saturated acid content, appears much less probable than one where a definite fraction of the fully saturated glyceride is always functioning. If the proportion of the trisaturated glyceride is related to the saturated acid content, the most likely relationship would be $GS_3 = K.S^3$.

We have already published a note[21] regarding one aspect of the question and a detailed examination of published data shows that K shows a maximum value in *Laurus nobilis* kernal fat,[22] where GS_3 is 41 and S^3 is 20·5 giving 2·02 as the value of K. Regarding the lower limit, it may be stated that it tends towards zero. Natural fats containing large proportions of myristic and lower saturated acids possess values for K in the neighbourhood of one, and are frequently of the positive type: the six palmæ fats showing a value for K within $1 \cdot 05 \pm 0 \cdot 02$, or the cow milk fats which give an average value of 1·11 for K. The internal depot fats of the land animals often belong to

the positive group, although they do not generally contain any appreciable proportions of lower saturated acids.

The most interesting aspect of the study is the constant K, the value of which is so specific, that the nature and proportions of saturated or unsaturated acids, or the position of the source in the scale of evolution or the special functions which fats are likely to have, does not seem to affect it. Vegetable seed fats, which have been considered as excellent examples of the operation of the rule of even distribution, show this relationship well. The fruit-coat fats do not generally obey the rule of even distribution as regards the proportion of fully saturated glycerides or the variations due to differences in saturated acid content. However, stilling asebifera fats typical fruit coat fat show the GS_3/S^3 relationships, K being 0·75. *Myristica molabarica* fat was considered to be anomalous, but on the basis of the present conception it shows K to be 0·92. It is clear from the tabulated data that irrespective of the theory[23] concerning their origin, the depot fats show the GS_3/S^3 characteristics. The cow milk fats give the most important confirmation of our hypothesis and provide the widest variation in saturated acid content for the same fat from the same biologic source so far examined. The manner of variation of fully saturated glycerides with saturated acid content, considered a very special and characteristic relationship exhibited by mammalian milk-fats, should be explained in any theory concerning the genesis of these fats. Graham, Houchin, Peterson and Turner[24] have suggested that fat metabolism in the mammary gland probably takes the form of synthesis rather than breakdown. A close examination shows that milk-fats show no outstanding peculiarity demanding a special theory, the fully saturated glyceride content of cow milk-fats[24] is given by the equation $(1 \cdot 12 \pm 0 \cdot 02).S^3$, for buffalo milk-fat the constant is 0·98 and for sheep milk-fat 0·90. It is interesting to note that the abnormality in the fatty acid composition, due to ingestion[25, 26] of foreign fats in the diet, does not affect the constant; and it is clear that it is not necessary to assume anything fundamentally characteristic of the origin of mammalian milk-fats to explain the peculiar trisaturated glyceride: saturated acid ratio; as it is now clear that the mammalian milk-fats do not form any exception to the ordinary rules obeyed by all the other natural fats.

Summary

A critical analysis of the trisaturated glyceride content of fats shows that the natural fats are characterised by definite numerical relationships between the proportions of GS_3 experimentally determined and those possible according to chance distribution and that the ratio between these is a specific characteristic of the source.

	Name of Fat	S	GS_2	S^3	K	Group
1.	*Cocos nucifera*[16] ..	93·9	86·0	82·8	1·04	Positive
		92·9	84·0	80·2	1·05	do
2.	He goat–back tissue fat[27] ..	63·1	29·2	25·1	1·16	do
	She goat– do ..	63·8	30·8	25·8	1·19	do
	Mutton tallow[16] ..	61·0	26·6	22·7	1·17	do
3.	Cow Milk Fat[16]—					
	(*a*) English spring pasture ..	61·9	27·2	23·7	1·16	do
	(*b*) do autumn feed ..	63·0	29·1	25·0	1·16	do
	(*c*) do stall feed, soybean ..	70·0	38·2	34·3	1·11	do
	(*d*) do do cocoanut cake ..	72·4	41·3	37·9	1·09	do
	(*e*) New Zealand spring pasture ..	70·2	39·6	34·6	1·15	do
	(*f*) Control ..	71·4	40·4	36·4	1·11	do
	(*g*) Control ..	64·1	34·2	33·0	1·04	do
	(*h*) Linseed oil in diet ..	61·3	24·8	23·0	1·08	do
	(*i*) Rape oil in diet ..	59·4	25·3	21·0	1·20	do
	(*j*) Cod-liver oil in diet ..	51·5	17·2	15·3	1·12	do
		50·6	14·6	12·9	1·13	do
4.	Buffalo milk-fats– Sample 1[29] ..	74·9	41·7	42·0	0·99	do
	2 ..	62·9	24·3	24·8	0·98	do
	3 (Ref. 30) ..	70·1	34·3	34·5	0·99	do
5.	*Manicraria saccifera*[16] ..	91·6	82·0	76·86	1·07	do
6.	*Abrocomia sclerocarpa*[16] ..	86·3	69·0	64·27	1·07	do
7.	*Astrocoryum tucuma*[16] ..	88·0	73·0	68·16	1·07	do
8.	*Elotis guinonsis*[16] ..	85·3	66·0	62·0	1·06	do
9.	Babassu kernal fat[20] ..	86·7	67·3	65·2	1·03	do
10.	*Myristica malabartca*[16] ..	59·2	19·0	20·7	0·92	Negative
		56·2	16·0	17·7	0·91	do
11.	*Stillingia sebifera*[16] ..	72·5	28·4	38·0	0·75	do
		68·4	23·9	32·0	0·75	
12.	Rat fat[16] ..	34·5	2·5	4·0	0·63	do
		37·0	3·5	5·0	0·70	do
13.	Indian ox depot: Calcutta[28] ..	67·5	28·0	30·75	0·91	do
	Bombay ..	72·9	36·0	38·7	0·93	do
14.	*Shorea stenoptera*[16] ..	62·9	5·1	24·9	0·20	do
		62·8	4·5	24·8	0·18	do

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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part I. The System: $KNO_3 - Pb(NO_3)_2 - H_2O$

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A SURVEY of literature reveals that no systematic attempt has been made to study the formation of complex compounds between lead nitrate and alkali nitrates.

Le Blanc and Noyes[1] appear to be the first to have noted that the solubility of lead nitrate in water at ordinary temperature is increased by the presence of potassium nitrate but decreased by sodium nitrate. The difference was ascribed to the existence of potassium nitrate in the solution as double molecules, and cryoscopic measurements were recorded in favour of this view. These observations were confirmed by A. Kanitz.[2]

Later Lewis[3] determined the solubility of a series of mixtures of lead nitrate with sodium and potassium nitrates respectively in water, and concluded that in the presence of sodium salt the solubility of lead nitrate was in agreement with Nernst's Law on the influence of a common ion, but in the case of potassium nitrate there was evidence for the formation of complex ions. He suggested the formation of a complex ion like $(K.PbNO_3)^{\cdot\cdot}$ according to the reaction:—

$$Pb(NO_3)_2 + KNO_3 \rightleftharpoons (K.PbNO_3)^{\cdot\cdot} + 2NO'_3$$

The addition of either sodium or potassium nitrate to a solution of lead nitrate causes a considerable diminution of the plumbous ions concentration, measured electromotively, as was pointed out by Lewis[3] and others thus indicating complex formation in each case, although to a greater extent with the potassium salt.

Miss Isaac[4] determined the saturation temperatures of the solutions containing varying amounts of lead nitrate and a fixed ratio of sodium or potassium nitrate to water. The abnormal behaviour in these two was attributed to some complex ion formation.

Glasstone and Harold N. Saunders[5] while studying the ternary systems: Lead nitrate-sodium nitrate-water and Lead nitrate-potassium nitrate-water, concluded that sodium nitrate in general causes a decrease in the solubility of lead nitrate while potassium nitrate causes the solubility of lead nitrate to increase. The difference in the behaviour between the two alkali nitrates was ascribed to the variation in the degree of complex ion formation and hydration. The conclusion was in agreement with that of Le Blanc and Noyes.

Considering the strong electro-positive nature of potassium according to the modern electronic theory of valency, the existence of a stable complex ion like $(K.PbNO_3)^{\cdot\cdot}$ suggested by Lewis would scarcely be expected so that Glasstone and Saunders gave the probable formula of the complex ion as $[Pb(NO_3)_4]''$.

Later Glasstone and E. J. Riggs[6] while studying the quaternary system: potassium nitrate-lead nitrate-barium nitrate-water, indicated the probable existence of a double salt, *viz.*, $2KNO_3$-$Pb(NO_3)_2$, in the form of a mixed crystal with the double salt $2KNO_3$-$Ba(NO_3)_2$.

G. Malquori[7], from measurements of conductance and viscosity of solutions of lead nitrate, of ammonium nitrate and of mixtures of these two salts at temperatures between 15° C.–60° C., adduced evidence for the existence of a complex of the type: $Pb(NO_3)_2$-$2NH_4NO_3$, giving rise probably to the ion $[Pb(NO_3)_4]''$.

K. Laybourn and W. M. Madgin[8] studied the systems in absence of water, as also W. F. Ehret, A. E. Hill and others[9] but found no complex formation in the solid state.

Thus the work done so far in aqueous solutions suggests the probable existence of one double or complex compound between lead nitrate and potassium nitrate and a similar one between lead nitrate and ammonium nitrate of formulæ:—$2KNO_3.Pb(NO_3)_2$ and $2NH_4NO_3.Pb(NO_3)_2$, but probably no such compound was formed in the absence of water. A systematic investigation with a view to confirm the above complex formation and to discover other complexes, if any, is desirable.

We have examined a number of physico-chemical-properties of the system: Lead nitrate-Alkali nitrate-water. The properties investigated were:—density, viscosity, rheochor, specific conductivity, surface tension, parachor, depression in freezing points, E. M. F., magnetic susceptibility, and transport number, all of which have yielded similar and unequivocal results leading to the same conclusions.

Experimental

The substances (B.D.H., A.R.) were recrystallised thrice, and stock *molar* solutions of lead nitrate and potassium nitrate were prepared in conductivity water. A small flask was blown and calibrated to hold 60 c.c. solution. 20 c.c. of potassium nitrate solution (1M.) were pipetted into the flask to which the requisite volume of lead nitrate (1 M.) was added and the mixture made up to the mark (60 c.c.) by addition of water. In this way 25 solutions were made in which the concentration of potassium nitrate remained the same (*viz.*, 1/3 M.), while that of lead nitrate varied systematically from 0·0 M. to 2/3 M.

These solutions were stored in steamed reagent bottles (100 c.c. capacity). Density at 30° C. was determined by pyknometer method. To determine the mean molecular weight the water content was estimated by evaporating to dryness a known weight of the solution.

I. Viscosity and Rheochor

The first property studied was viscosity which was determined by means of an Ostwald viscometer (Findlay: *Pract. Phys. Chemistry*). Precautions were taken in cleaning the viscometer with chromic acid mixture each time after the experiment, and in maintaining the temperature at 30° C. $\pm$ 0·05° C. From viscosity the rheochor values were calculated in each case by using the formula:—

$$Rh = \frac{M\eta^{\frac{1}{3}}}{D}$$ (where M = Mean molecular weight, η = viscosity and D = Density).

The values of viscosity and rheochor* are given in Table I.

The solutions were of the following composition.

Solution Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
C.C. Pb $(NO_3)_2$ added to 20 cc. KNO_3	0cc.	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40

* Limitations of the applicability of Parachor and Rheochor are well known. They are, however, easy to carry out and very useful, especially for diagnostic purposes.

TABLE I. *Viscosity and Rheochor*

Temperature : 30° C ± 0·05° C

Soln.No	Density	Viscosity*	Rheochor	Soln.No	Density	Viscosity*	Rheochor
1	1·0204	0·9919	18·168	14	1·1049	1·0722	18·445
2	1·0297	1·0061	18·18	15	1·1145	1·0722	18·445
3	1·0344	1·0116	18·19	16	1·1237	1·0904	18·54
4	1·0391	1·0123	18·205	17	1·1331	1·1010	18·58
5	1·0438	1·0103	18·20	18	1·1426	1·1117	18·62
6	1·0488	1·0185	18·23	19	1·1517	1·1190	18·67
7	1·0535	1·0242	18·25	20	1·1613	1·1279	18·71
8	1·0582	1·0305	18·27	21	1·1705	1·1359	18·75
9	1·0631	1·0325	18·28	22	1·1797	1·1438	18·79
10	1·0678	1·0318	18·28	23	1·1890	1·1520	18·82
11	1·0771	1·0465	18·335	24	1·1980	1·1605	18·85
12	1·0861	1·0585	18·39	25	1·2070	1·1682	18·88
13	1·0953	1·0684	18·44				

* Viscosity values here mean relative viscosity *i.e.*, (H_2O=1).

When these values are plotted against the volume of lead nitrate added, we obtain the various curves shown in Fig. 1. It will be observed that in

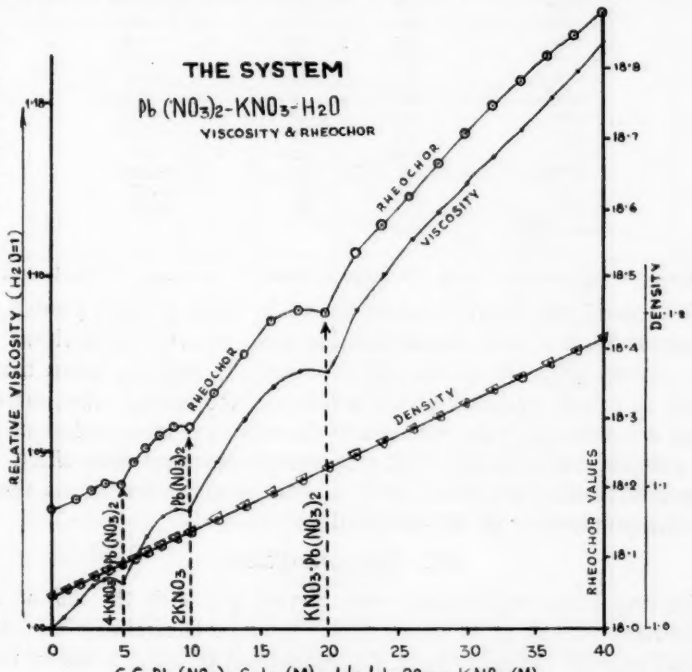

FIG. 1

both cases there are breaks in the curves at concentrations corresponding to 5 c.c., 10 c.c. and 20 c.c. of $Pb(NO_3)_2$. The molecular ratios between $Pb(NO_3)_2$ and KNO_3 at these points correspond to the compounds of formulæ: $4KNO_3.Pb(NO_3)_2$; $2KNO_3.Pb(NO_3)_2$ and $KNO_3.Pb(NO_3)_2$.

II. Conductivity

Measurements of conductivity were made at 30° C. by Kohlrausch's method. The conductivity cell used was of pyrex glass with platinum electrodes each of area about 1 sq. cm., and inter electrode distance about 12 cm., the cell constant being 24·25. At least three readings were taken for each solution, usually when the null point was near, or exactly at the centre of the bridge.

TABLE II. *Specific Conductivity*

Cell constant : 24·25 Temperature : 30° C ± 0·05° C.

Soln.No.	Specific Cond. × 10^{-2}	Resistance*	Soln. No.	Specific Cond. ×10^{-2}	Resistance*
1	3·9656	611	14	6·5690	369
2	4·3147	562	15	6·9950	348
3	4·5080	537	16	7·0798	343
4	4·7074	515	17	7·2750	333
5	4·9498	490	18	7·5260	322
6	5·0273	483	19	7·7200	314
7	5·1340	472	20	7·8990	307
8	5·3080	457	21	8·0720	300
9	5·5170	440	22	8·2414	294
10	5·7590	421	23	8·3980	289
11	5·8170	416	24	8·5570	284
12	5·9890	404	25	8·6990	279
13	6·2560	388			

* Refers to the resistance when null point is exactly at the centre of the bridge.

The specific conductivity values shown in Table II when plotted against the concentration of lead nitrate solution yield a curve which shows exactly similar breaks (Fig. 2), at the same points. It may be noted that while viscosity is a bulk property of the solute and the solvent taken together, in the case of conductivity the influence of the solvent is more or less eliminated being constant and negligible and only the solutes exert their effect. When two such dissimilar properties yield similar results, there is no reason to doubt the genuineness of the observation.

III. Freezing-Point

Freezing point experiments were carried out with the aid of a wide thermos-flask serving as an outer bath. In order to minimise the variation of temperature of the outer bath, the proportion of ice and salt in the bath was also kept the same.

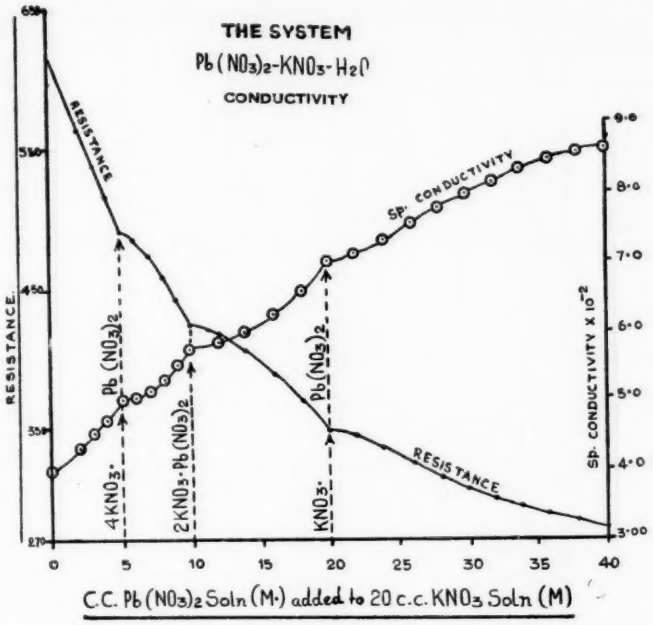

FIG. 2

TABLE III. *Depression in Freezing-Point*

Soln. No.	ΔF. Point	Soln. No.	ΔF. Point	Soln. No.	ΔF. Point
1	1·0600	8	1·4300	15	1·8125
2	1·1425	9	1·4675	16	1·9440
3	1·1870	10	1·4625	17	2·0275
4	1·2450	11	1·5600	18	2·1200
5	1·2720	12	1·6500	19	2·2000
6	1·3200	13	1·7200	20	2·2900
7	1·3700	14	1·7725		

Fig. 3 shows the values of depression in the freezing points of the solutions, plotted against the volume of $Pb(NO_3)_2$ added. This graph leads to further confirmation of previous results by showing three breaks at the same concentrations.

DISCUSSION

These curves appear a little difficult to interpret as they are different in type from the phase rule diagrams, where a sharp minimum is associated with a eutectic point, while the compound formation is very often indicated

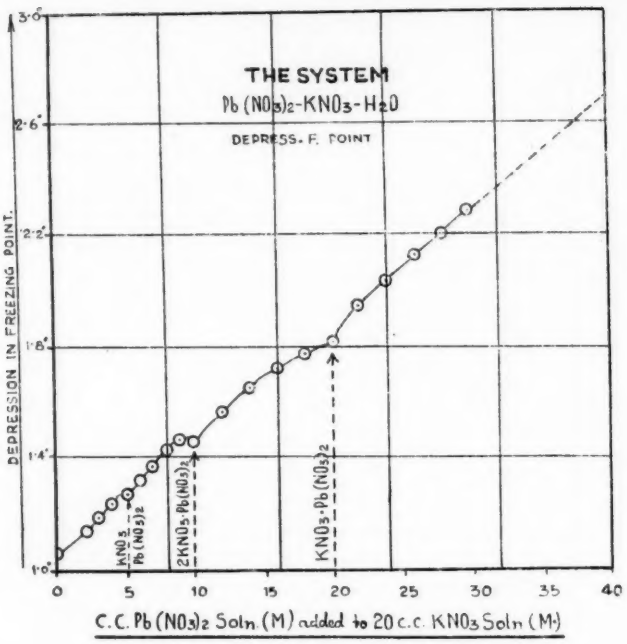

FIG. 3

as a smooth maximum. But it is obvious that the phase rule is not applicable to our results, since we are dealing with the properties in a single phase system. Further the conditions of the experiment are so chosen that the effect of variation of the concentration of a single constituent is obtained as a sharp maximum or a kink in the curve.[10] This effect is revealed much more convincingly when dp/dc, the change in the measured property per c.c. of the added constituent, is plotted against concentration (Fig. 4).

The interpretation of the curves will be more satisfactory when we carry out exactly similar experiments with the constituents of a known complex compound and then by analogy we can arrive at the right conclusion. The results of such an experiment are described in the next part of this series.

For the present, if it be assumed that the kinks occur at the stoichiometric proportions corresponding to the different complexes existing in solution we may conclude that the two salts KNO_3 and $Pb(NO_3)_2$ form the compounds corresponding to the formulæ:—

$4KNO_3.Pb(NO_3)_2$, $2KNO_3.Pb(NO_3)_2$ and $KNO_3.Pb(NO_3)_2$,

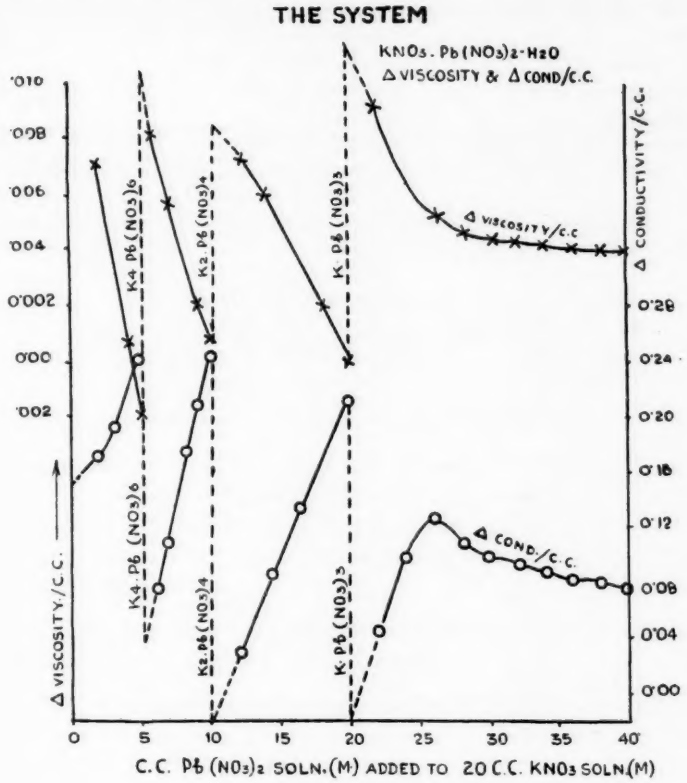

FIG. 4

in which at this stage we do not express any opinion about their constitution or structure. It may be noted that only one of these compounds, *viz.*, $2KNO_3.Pb(NO_3)_2$ has been known or suspected before.

The authors record their thanks to Professor P. S. MacMahon, Head of the Department of Chemistry, who suggested this problem and offered valuable criticisms and suggestions in the course of the work.

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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part II. The Systems: (a) $NaNO_3$-Pb $(NO_3)_2$-H_2O (b) KNO_3-$AgNO_3$-H_2O

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ENOUGH experimental evidence has been adduced to indicate the possible formation of complex compounds between lead nitrate and potassium nitrate in aqueous solution in the previous paper, and the presence of three definite complexes has been assumed. In this paper we describe the results obtained with two systems:

(*a*) *lead nitrate-sodium nitrate-water*:—where there is no indication of the formation of any complex compound, and

(*b*) *silver nitrate-potassium nitrate-water*:—in which a complex compound is definitely known to be produced. ("General and Inorganic Chemistry" by J. R. Partington, Edition 1946, page 349).

EXPERIMENTAL

I. The system: Lead nitrate-sodium nitrate-water:

Exactly the same number of solutions were prepared and similar procedure adopted as described in Part I.

The solutions had the following composition.—

Solution Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
C.C. Pb $(NO_3)_2$ added to 20 cc. $NaNO_3$	0cc.	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40

The properties investigated were specific conductivity and viscosity. The values are given in the following Table,

TABLE I

Specific Conductivity

Cell constant : 24·25 Temperatute : 30 ± 0·05°C.

Soln. No.	Sp. Cond. × 10^{-2}	Soln.No.	Sp. Cond. × 10^{-2}	Soln.No.	Sp. Cond. × 10^{-2}
1	3·258	10	5·010	19	7·187
2	3·655	11	5·3328	20	7·381
3	3·868	12	5·609	21	7·590
4	4·0335	13	5·852	22	7·788
5	4·233	14	6·084	23	7·965
6	4·390	15	6·3314	24	8·149
7	4·552	16	6·552	25	8·308
8	4·712	17	6·7726		
9	4·877	18	6·986		

TABLE II

Viscosity and Density

Temperature : 30 ± 0·05°C.

Soln.No.	Density	Viscosity*	Soln.No.	Density	Viscosity*
1	1·0183	1·0198	14	1·1024	1·0947
2	1·0277	1·0283	15	1·1118	1·1021
3	1·0324	1·0325	16	1·1211	1·1110
4	1·0371	1·0367	17	1·1304	1·1187
5	1·0418	1·0406	18	1·1398	1·1278
6	1·0464	1·0448	19	1·1491	1·1362
7	1·0511	1·0490	20	1·1585	1·1450
8	1·0558	1·0532	21	1·1678	1·1537
9	1·0604	1·0574	22	1·1771	1·1618
10	1·0651	1·0616	23	1·1865	1·1702
11	1·0744	1·0696	24	1·1958	1·1785
12	1·0838	1·0780	25	1·2005	1·1865
13	1·0931	1·0863			

* The viscosity values are relative *i.e.*, ($H_2O = 1$).

As explained in Part I, the concentration of sodium nitrate was kept constant (*viz.*, 1/3 M.), while that of lead nitrate varied from 0·0 M. to 2/3 M. The plots (Figs. 1 and 2) illustrate the variation of the property investigated corresponding to the variation of the concentration of lead nitrate. It is interesting to note that in this case all the plots are regular without any breaks, which may be interpreted to mean that the tendency for the formation of complex compounds between these two salts is practically nil, in conformity with the conclusions arrived at by Le Blanc and Noyes,[1] and Glasstone and Saunders.[2]

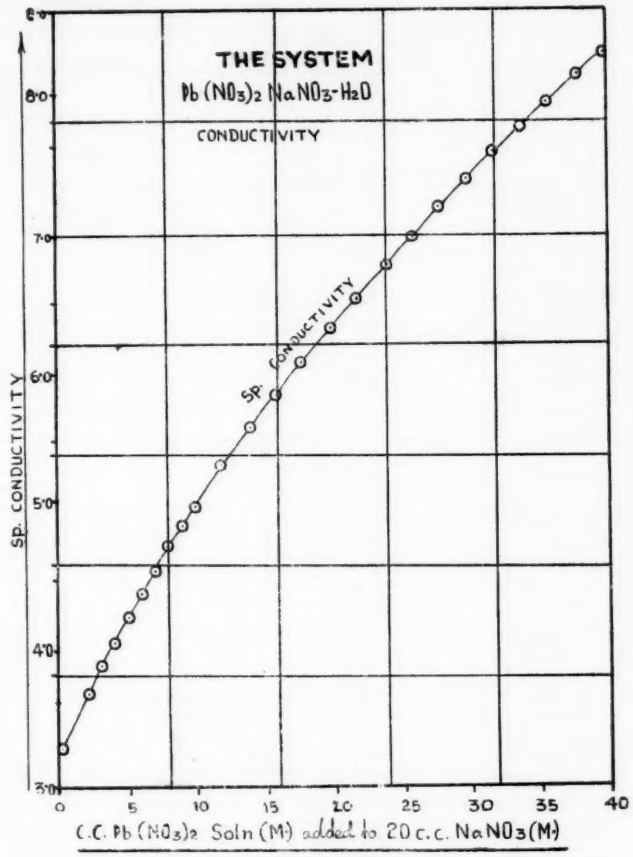

FIG. 1

II. The system: KNO_3-$AgNO_3$-H_2O

The formation of one compound, *viz.*, ($AgNO_3.KNO_3$), has been definitely established by a number of authors.[3] The main object of our re-examining this system is to ensure that our methods of procedure are correct and yield the same results, as obtained by other authors following different methods.

Molar solutions of extra pure silver nitrate and potassium nitrate (B.D.H., A.R.) were prepared. A set of 25 solutions was made in which the strength of KNO_3 was kept constant (*viz.*, 1/3 M.), while that of $AgNO_3$ varied systematically from 0·0 M to 2/3 M. as explained in the previous

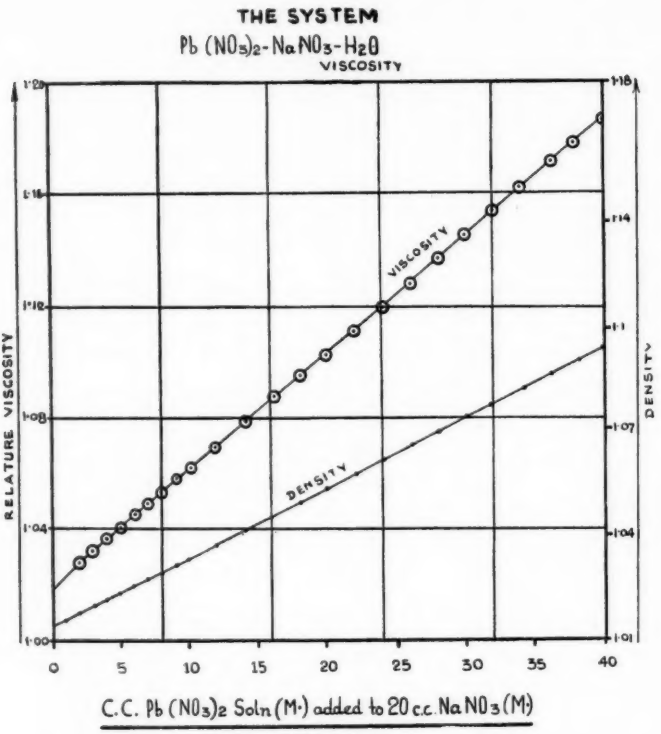

FIG. 2

section. The properties studied were density, viscosity and E.M.F. The values of density and viscosity are given in the following table.

TABLE III

Density and Viscosity

Temperature : 25 ± 0·05°C.

Soln.No.	Density	Viscosity*	Soln.No.	Density	Viscosity*
1	1·0337	1·0070	14	1·1356	1·0543
2	1·0450	0·9830	15	1·1469	1·0622
3	1·0506	0·9910	16	1·1582	1·0792
4	1·0563	0·9960	17	1·1696	1·0876
5	1·0620	1·0000	18	1·1809	1·0963
6	1·0676	1·0046	19	1·1922	1·1051
7	1·0733	1·0080	20	1·2036	1·1141
8	1·0790	1·0120	21	1·2149	1·1230
9	1·0846	1·0165	22	1·2262	1·1321
10	1·0903	1·0199	23	1·2375	1·1412
11	1·1016	1·0284	24	1·2488	1·1497
12	1·1129	1·0374	25	1·2601	1·1587
13	1·1243	1·0459			

* The viscosity values are relative, *i. e.*, (H_2O = 1).

When these values are plotted against the volume of silver nitrate added, the curve represented in Fig. 3 is obtained which shows one break at 10 c.c.

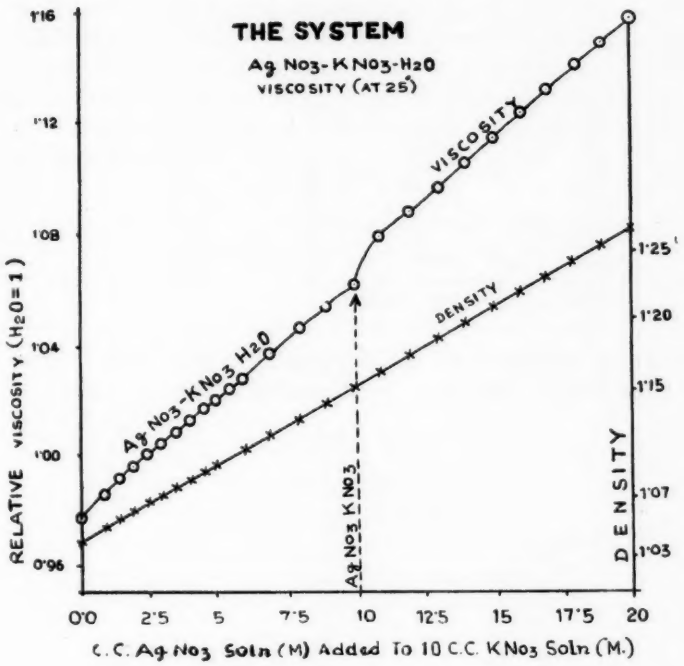

FIG. 3

The molecular ratio between silver nitrate and potassium nitrate at this point corresponds to the compound: ($AgNO_3$-KNO_3).

Additional confirmation of these results is afforded by measurements of E.M.F., which were obtained by using the following type of cell:

Ag	$AgNO_3$ Soln.	Saturated	Hg_2Cl_2	Hg
	KNO_3 Soln.	KNO_3 Soln.	N.KCl Soln.	

The values of E.M.F. are given in Table IV.

TABLE IV

(*E.M.F.*)

Room Temperature (About 20°C.)

Soln.No.	E. M. F.	Δ E. M. F./CC.	Soln.No.	E. M. F.	Δ E. M. F./CC.
1	0·0300(volts)	..	14	0·4660	0·001
2	0·4130	0·3830	15	0·4660	0·000
3	0·4240	0·0110	16	0·4720	0·003
4	0·4310	0·0070	17	0·4740	0·001
5	0·4354	0·0044	18	0·4750	0·0005
6	0·4390	0·0036	19	0·4760	0·0005
7	0·4430	0·0034	20	0·4770	0·0005
8	0·4462	0·0032	21	0·4778	0·0004
9	0·4492	0·0030	22	0·4788	0·0004
10	0·4520	0·0028	23	0·4794	0·0004
11	0·4570	0·0025	24	0·4802	0·0004
12	0·4610	0·0020	25	0·4810	0·0004
13	0·4640	0·0015			

The change of E.M.F. per c.c. (column 3), at each concentration brings out the effect better. The plots illustrate the nature of change (Fig. 4).

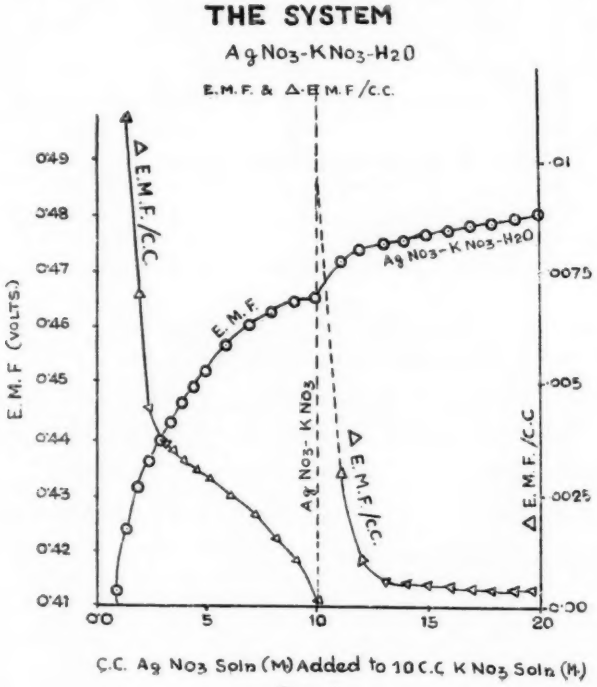

FIG. 4

Both the curves reveal the transition point at a concentration corresponding to the compound $AgNO_3.KNO_3$.

Conclusion

The differences in the results obtained with the two systems:—$Pb(NO_3)_2$-$NaNO_3$-H_2O and $AgNO_3$-KNO_3-H_2O, examined enable us to say definitely that the methods of procedure followed by us are such as to reveal the formation or otherwise of complex compounds in solution, and that in the case of positive results the formula of the compound produced can be directly read from the graph.

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2. Glasstone and Saunders .. *J. C. S.*, 1923, **2**, 2134.
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NON-ASSOCIATION OF CHEMICAL CHANGE WITH THE HIGH FREQUENCIES IN THE ELECTRICAL DISCHARGE

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(Communicated by Professor S. S. Joshi, D.Sc. (London), F.A.Sc., F.R.I.C.)

In his classical researches on the formation of ozone in the silent electric discharge through an ozonizer, Warburg[10] tried to relate the amount of chemical change with the corresponding electrical energy consumed. Warburg measured the current flowing through the ozonizer by two different methods, *viz.*, (i) by means of a thermal junction and galvanometer, and (ii) by determining with a quadrant electrometer the potential drop over part of a high resistance connected to ground. He found that an alternating potential applied to an ozonizer creates "higher harmonics" (10^5–10^6 per sec.) in the circuit, which, according to him, do not contribute to the ion current and hence do not cause chemical reaction. The thermal junction measures the total current due to the fundamental and the "higher harmonics", whilst the quadrant electrometer measures the fundamental current only, especially if a by-pass condenser is included in the circuit. Warburg found that the rate of ozone formation increased ten times as the fundamental frequency was varied from 50 to 500 cycles per second, whereas the strength of the harmonics increased in a much smaller ratio; hence his conclusion that the "higher harmonics" do not contribute to the chemical effect.

Warburg's views regarding the ineffectiveness of the "higher harmonics" to bring about chemical change receive confirmation from a rather unexpected direction. The recently discovered *Joshi-Effect*[2] affords a basis for the evaluation of the role of the "higher harmonics" with respect to the chemical change occurring in the ozonizer.

It should be mentioned at this stage that in the light of recent work Warburg does not seem to be quite correct in calling the higher frequencies present in the ozonizer discharge "higher harmonics of the order of 10^5–10^6 per sec." Examination of the discharge by Klemenc, Hintenberger and Höfer[7] by means of the cathode-ray oscillograph indicates that the current through the ozonizer comprises strong pulses of short duration occurring every half a cycle of applied A.C. potential. No high frequency oscillations could be detected by them.

Similar are the findings of Joshi[3] who investigated the current structure and its time-delineation by means of the cathode-ray oscillograph. The oscillograph revealed, besides the frequency of the A.C. supply, "a remarkably large number of higher frequencies of widely varying strengths; they were not transients but repeatable and characteristic constituents of the discharge current, *i*." Now, with the discharge on, if the ozonizer is irradiated, the *Joshi-Effect*, *i.e.*, an instantaneous and reversible diminution in the discharge current, $-\Delta i$, is observed. Under these conditions, the oscillograms of the discharge current obtained by Joshi reveal an instantaneous and reversible diminution or suppression of the amplitudes of the higher frequencies, leaving chiefly the simplified pattern of the fundamental frequency. That, as a general finding, the high frequencies constitute by far the major source of this phenomenon is shown by Joshi's subsequent results,[4] Tiwary's data[9] for various wave bands in the region 10 to 2,400 metres wave-length, and the findings of other workers in these Laboratories, observed with other gases and using widely varied modes of current detection.

The fact that the amplitudes of the higher component frequencies of the discharge current are suppressed or diminished markedly on irradiating

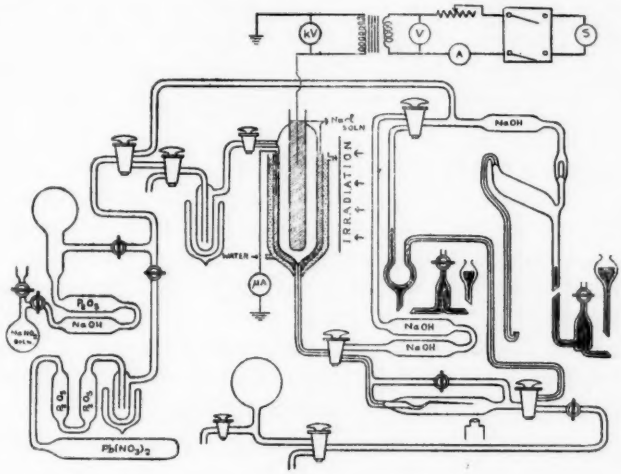

FIG. 1.

the ozonizer constituting the *Joshi-Effect*, $-\Delta i$, was utilized in the experiments herein reported, in order to see whether these high frequencies contribute in any measure to the chemical action occurring in the silent electric discharge, the reaction studied being the decomposition of nitrogen peroxide.

Description of the Apparatus

(*cf.* Fig. 1)

Gas generator and gas holder.—Dry lead nitrate was taken in a hard glass tube closed at one end and joined on the other to a pair of liquid air traps through a series of drying tubes containing fused $CaCl_2$ and P_2O_5. This portion of the apparatus could be separately evacuated by means of a High-vac. Cenco pump and a topler pump.

In order to prepare and store the gas NO_2, the above part of the apparatus was first thoroughly evacuated. The liquid air traps were kept immersed in Dewar flasks containing liquid air. The lead nitrate tube was covered with a copper wire gauze and carefully heated. After a sufficient amount of gas had condensed in the liquid air traps, the oxygen and other uncondensed fraction of the gas were pumped out by means of the topler pump. The liquid air was now removed and the solidified gas in the liquid air trap allowed to vaporize. Dry air was then admitted into the apparatus and allowed to mix with the gas, in order to convert any NO or N_2O_3 into NO_2. The gas was again solidified under liquid air and the uncondensed gases were pumped out. The above process was repeated several times till at length the solidified N_2O_4 was straw yellow in colour and no blue tinge indicating the presence of NO or N_2O_3 was visible. Since the gas cannot be stored for any length of time owing to its action on the stop-cock grease, it was kept in the solid state and vaporized only when required for experiment.

The Reaction Vessel.—A Siemen's glass ozonizer was used as the reaction vessel. It was connected at the top to the gas holder and at the bottom to a glass-spoon manometer of the type used by Jackson.[1] The spoon manometer was used as a null instrument; when the glass index of the spoon was deflected as a result of variation of pressure in the reaction vessel, the pressure of air in the outer jacket of the spoon was varied till the index came back to the initial position, which was ascertained by means of a microscope. Then the pressure in the outer jacket was read by means of a mercury manometer which gave readings correct to 0·5 mm. Hg.

Electrical Connections.—Single phase alternating current of frequency 100 cycles per second was obtained from a rotary converter and was fed into the primary of a step-up transformer to give a secondary potential of the required kV measured by means of a kilo-voltmeter. The voltage was kept constant at the required value by hand regulation of some rheostats included in the primary circuit which also included a switch. One terminal of the transformer was introduced into the inner tube of the ozonizer containing

some electrolyte (NaCl solution). The other terminal of the transformer was earthed. The outer terminal of the ozonizer, which was a glass jacket containing the same electrolyte was connected to a rectifier type milliammeter and then to earth.

Irradiation of the Ozonizer.—Two 200-watt bulbs were mounted on an upright inside a wooden box. The side of the box facing the ozonizer was of the nature of a movable shutter. In order that the gas in the ozonizer might not absorb the heat rays of the bulbs, a glass jacket through which cold water was circulated, surrounded the ozonizer.

Experimental Procedure and Results

The following experiment was conducted in order to see whether the *Joshi-Effect* is given by a compound gas such as NO_2. NO_2 at a definite initial pressure was introduced into the annular space of the ozonizer and subjected to an alternating potential of 5 kV (r.m.s.). The progress of the reaction was followed by noting the time-variation of the discharge current and of the pressure of the reaction mixture. The current was measured by means of a Weston rectifier-type milliammeter (range 0–1 milliamp.) reading correct to 0·02 of a milliamp. In order to observe the occurrence of the *Joshi-Effect*, as soon as the current in the dark was read, the shutter of the box containing the two electric bulbs kept already lighted was raised and the ozonizer irradiated for an instant. The current suffered an instantaneous diminution, which was recorded and then the shutter was lowered back into position, thus cutting off the light. The whole operation did not take more than a few seconds. The following table is typical of one group of data obtained in these experiments.

Table I

Initial pressure of NO_2 : 11·6 cm.
Applied potential : 5 kV (r.m.s.)

Time of discharge in minutes	Pressure of gas in cm.	Discharge current in m. amp. (in dark)	(in light)
0	11·6		
1·5		0·64	
4		0·64	
8		0·64	0·62
10		0·65	0·63
15		0·65	0·63
17	13·9		
18·5		0·71	0·69
20		0·75	0·73
21		0·77	0·74
22		0·78	0·75
24	13·4	0·79	0·76
26		0·70	0·75
30	13·1	0·80	0·77

It is seen from the above table that the *Joshi-Effect* occurs definitely in NO_2. It may also be stated that this constitutes the first instance of the observation of this phenomenon in a compound gas like NO_2. Since most of the current was diverted through a shunt—a rheostat of 93 ohms—and since the current was measured by means of a rectifier type milliammeter, an instrument not so sensitive as a thermal junction and galvanometer, the magnitude of the *Joshi-Effect* is not brought out to the full extent. Still that the effect is given to an appreciable extent is unmistakable.

That the magnitude of the *Joshi-Effect* is governed by several factors such as the applied potential, nature of the current detector, gas pressure, nature of solid-gas interface and electrical quantities, *e.g.*, the inter-electrode capacitance, wave form and current frequency, etc., has been emphasised by Joshi.[5] Hence how far the extent of the *light-effect* in NO_2 is modified by lower applied potentials was next investigated.

The experiment was conducted as follows. NO_2 at a definite initial pressure was sealed in the ozonizer and subjected to alternating potentials of 2·1 kV (r.m.s.), *i.e.*, near about the threshold potential. The ozonizer

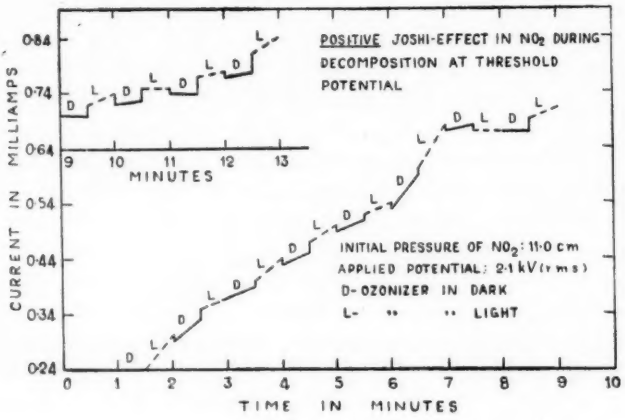
POSITIVE JOSHI-EFFECT IN NO2 DURING DECOMPOSITION AT THRESHOLD POTENTIAL
INITIAL PRESSURE OF NO2 : 11·0 cm
APPLIED POTENTIAL : 2·1 kV (r m s)
D- OZONIZER IN DARK
L- " " LIGHT
CURRENT IN MILLIAMPS
TIME IN MINUTES
MINUTES

FIG. 2

was kept alternately in the dark and irradiated by two 200-watt electric bulbs for half a minute and the current read at the beginning and end of every half a minute interval. Since the current was low enough, no shunt was necessary for the milliammeter. One typical set of data obtained is given in Table II.

TABLE II

(*cf.* Fig. 2)

Influence of light on the discharge current during NO_2 decomposition near threshold potential

Initial pressure of NO_2 : 11·0 cm.

Applied potential : 2·1 kV (r.m.s.)

Ozonizer in	Time of discharge in minutes	Current in milliamps. (initial)	(final)
Dark ..	0–½	0·24	0·24
Light ..	½–1	0·24	0·24
D ..	1–1½	0·24	0·24
L ..	1½–2	0·24	0·30
D ..	2–2½	0·29	0·33
L ..	2½–3	0·35	0·37
D ..	3–3½	0·37	0·39
L ..	3½–4	0·40	0·44
D ..	4–4½	0·43	0·45
L ..	4½–5	0·47	0·50
D ..	5–5½	0·49	0·51
L ..	5½–6	0·52	0·54
D ..	6–6½	0·53	0·59
L ..	6½–7	0·60	0·68
D ..	7–7½	0·67	0·68
L ..	7½–8	0·67	0·67
D ..	8–8½	0·67	0·67
L .	8½–9	0·69	0·71
D .	9–9½	0·70	0·70
L ..	9½–10	0·72	0·74
D ..	10–10½	0·72	0·73
L ..	10½–11	0·75	0·75
D ..	11–11½	0·74	0·74
L ..	11½–12	0·77	0·78
D ..	12–12½	0·78	0·78
L ..	12½–13	0·81	0·84

Final Pressure of Gas = 11·7 cm.

It is seen from the above table and Fig. 2, that while the discharge current shows a photo-diminution at 5 kV (r.m.s.), a photo-increase in current is obtained at potentials near about the threshold value. It was also found that below the threshold potential, there was no effect of light on the current.

In the following experiments, NO_2 was taken in the ozonizer at a definite initial pressure and subjected to an applied potential of 5 kV (r.m.s.), the ozonizer being kept in the dark by enclosing it in a box. The time-variations of the pressure and current were noted till the pressure and current reached a constant value, indicative of either complete decomposition of the gas or an equilibrium-like steady state in the ozonizer. Next, the

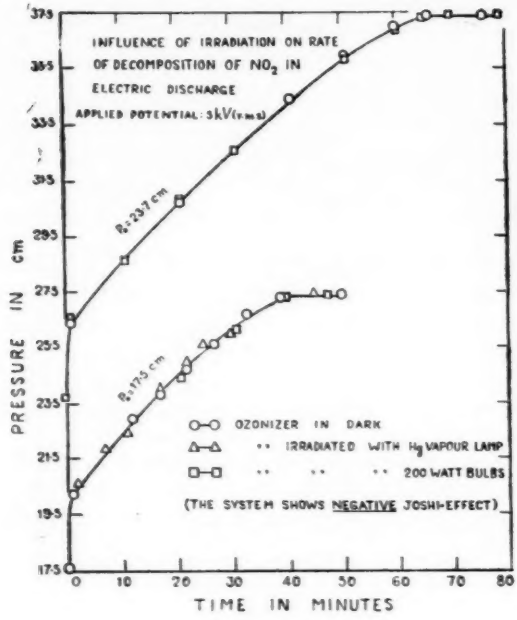

FIG. 3

TABLE III

(*cf.* Fig. 3)

Initial pressure of NO_2 : 17·6 cm.
Applied potential : 5 kV (r.m.s.)

Time in minutes	In dark		In Hg vapour lamp		In 200-watt bulbs light	
	Pressure cm.	Current m. amp.	Pressure cm.	Current m. amp.	Pressure cm.	Current m. amp.
0 ..	17·6	0·15	17·5	0·15	17·5	0·13
1 ..	20·2	0·16	..	..	20·1	0·14
2 ..	..	..	20·6	0·16	..	..
7 ..	..	..	21·8	0·16	..	..
10 ..	..	0·18	..	..	..	..
11 ..	..	..	22·4	0·16	..	..
12 ..	22·9	0·17	23·0	0·17	..	..
17 ..	23·8	0·17	24·0	0·17	..	..
21 ..	..	..	..	..	24·4	0·16
22 ..	24·7	0·17	24·9	0·18	..	..
25 ..	..	..	25·6	0·18	..	..
27 ..	25·6	0·17	..	..	..	..
30 ..	..	0·18	26·0	0·18	..	..
31 ..	..	..	..	..	25·9	0·16
33 ..	26·7	0·18	26·8	0·18	..	..
39 ..	27·3	0·18	27·4	0·18	..	..
40 ..	..	..	..	..	27·3	0·17
45 ..	27·4	0·19	27·4	0·18	27·4	0·18
50 ..	27·4	0·18	27·4	0·18	27·4	0·17

same initial pressure of the gas was subjected to the same potential of 5 kV (r.m.s.) and the above experiment repeated, but this time the ozonizer was kept irradiated throughout the reaction with light from a quartz mercury vapour lamp. A third run under the same conditions of pressure and applied potential was taken, this time the ozonizer being irradiated with light from two 200-watt bulbs. The data obtained are tabulated in Tables III and IV.

TABLE IV

(*cf.* Fig. 3)

Initial pressure of NO_2 : 23·7 cm.

Applied potential : 5 kV (r.m.s.)

Time in minutes	In dark		In Hg vapour lamp		In 200-watt bulbs light	
	Pressure cm.	Current m. amp.	Pressure cm.	Current m. amp.	Pressure cm.	Current m. amp.
0 ..	23·7	0·13	23·8	0·13	23·7	0·13
1 ..	26·4	0·14	26·5	0·15	26·5	0·14
6 ..	..	0·14	..	..	..	..
11 ..	28·6	0·15	28·7	0·16	28·6	0·15
21 ..	30·7	0·16	30·8	0·16	30·8	0·16
31 ..	..	..	32·7	0·17	32·6	0·16
41 ..	34·4	0·19	34·5	0·19	..	..
51 ..	35·9	0·19	35·9	0·19	35·8	0·18
60 ..	37·0	0·19	..	..	36·9	0·19
61 ..	..	..	37·2	0·20	..	..
65 ..	..	..	37·4	0·20	37·3	0·20
66 ..	37·4	0·20	..	..	..	..
70 ..	..	..	37·5	0·20	37·4	0·20
76 ..	37·4	0·20	..	..	..	..
80 ..	..	..	..	..	37·4	0·20

DISCUSSION OF RESULTS

It is seen from Table I that the *Joshi-Effect* is given by NO_2 to the extent of 4 to 5%, at an initial pressure of 11·6 cm. and applied potential of 5 kV (r.m.s.). It has also been observed in the course of these experiments that the greater the size of the ozonizer, *i.e.*, surface to volume ratio, and smaller the initial pressure and higher the applied potential and hence the discharge current, the greater is the magnitude of the net *Joshi-Effect*. It is also striking to observe from Table I that the *Joshi-Effect* is independent of any reaction that may be taking place in the ozonizer, for it is seen to persist throughout the progress of the reaction. How far the nature of the end products of the reaction will affect the magnitude of the *Joshi-Effect* as compared to NO_2 which, like Cl_2, is a gas with large electron affinity, is a moot point which requires further investigation.

The occurrence of photo-increase in the current at potentials near the threshold value is interesting (*cf.* Table II and Fig. 2). Similar positive effect, $+\Delta i$, has been observed in several cases " under insufficiently understood conditions such as special coating materials on the annular walls of the ozonizer, *e.g.*, with $KI_3 + KI$ mixture, vapours of iodine, phosphorus and sulphur; an abnormal working of a metal oxide type detector; spontaneously, after long 'aging' at a constant V in a semi-ozonizer excitation, etc.; a low applied V would appear to favour $+\Delta i$ under these conditions."[6] The transition $+\Delta i \rightleftharpoons -\Delta i$ is found to be potential reversible.

That the observed effect of light on the discharge current was really to be identified with the *Joshi-Effect* and was not due to any dissociation of the gas NO_2 was established in the following way; for, Norrish[8] has shown that illumination of NO_2 by means of a Hg-vapour lamp produces a slow increase in pressure which he attributes to the photochemical reaction $2NO_2 \rightarrow 2NO + O_2$. NO_2 was admitted into the ozonizer at some initial pressure and irradiated for 30 minutes with two 200-watt bulbs; no rise in pressure indicative of any dissociation was observed. The gas was then irradiated with a Hg-vapour lamp; here again, no rise in pressure was noted. The pressure was absolutely constant throughout the time of irradiation. No doubt the ultra-violet rays and the heat rays are cut off by the glass walls and the water jacket respectively. Thus it is clear that the change in the current during the electric discharge consequent on irradiating the ozonizer cannot be due to any chemical reaction initiated by light. Further if any reaction were to be started by light, it is difficult to see why it should give a positive effect at 2·1 kV and a negative effect at 5 kV. It is also pertinent to remark that the photo-change in current observed, being instantaneous and reversible, cannot be the concomitant of any reaction brought about by light, since the latter is essentially a time-continuous process and the current also may be expected to show a similar behaviour.

Having shown above that NO_2 throughout its decomposition in the silent electric discharge at 5 kV (r.m.s.) gives the *Joshi-Effect* and keeping in mind the fact that irradiating the ozonizer with visible light results in the suppression of the higher frequencies of the alternating current as is revealed by Joshi's oscillograms (*Nature*, *loc. cit.*), it would be easy enough to design an experiment with a view to testing the validity of Warburg's assumption that the higher frequencies do not cause chemical effect. This is what has been attempted above and the data obtained are given in Tables III and IV (*cf.* Fig. 3). If the higher frequencies were to contribute to the chemical effect, a distinct slowing down of the rate of the reaction and hence a longer

time for complete decomposition of the gas is to be expected when the discharge is carried out with the ozonizer kept irradiated throughout, than will be the case when the ozonizer is kept in dark. It is seen from Tables III and IV (Fig. 3) that there is practically no difference in the time for complete decomposition in the two cases, though the time of total decomposition is as high as 40 and 60 minutes respectively in the two series. The two curves lie very close to each other indicating thereby that, whether the high frequencies are present as in the case when the reaction is carried on in the dark or they are absent or suppressed as in the case when the ozonizer is irradiated, the rate and extent of chemical change are the same in both cases, thus leading to the conclusion that Warburg's view that the higher frequencies do not contribute to the chemical change receives corroboration from an altogether different line of evidence.

It is seen in Tables III and IV that the values of the current in the dark and on irradiation are almost the same. This is really due to the low value of the current as measured by the rectifier milliammeter. If a shunt with a higher resistance than the one used in these experiments had been attached to the milliammeter, the fall in the value of the current, $-\Delta i$, on irradiation, would have been more obvious. This was not possible owing to the low range (0–0·5 m. amp.) of the available milliammeter.

The author wishes to express his grateful thanks to Dr. S. S. Joshi, University Professor of Chemistry, Benares Hindu University, for his kind interest in this work and for helpful discussions. His thanks are also due to Mr. R. Jayaraman, M.Sc., Assistant Professor of Physical Chemistry and Assaying, College of Mining and Metallurgy, for help in the accumulation of data included in Tables III and IV.

Summary

NO_2 during decomposition by the silent electric discharge at 5 kV (r.m.s.) gives the negative *Joshi-Effect*, *i.e.*, an instantaneous and reversible diminution, $-\Delta i$ of 4 to 5% in the discharge current on irradiating the ozonizer with visible light. The effect is given at all stages of the decomposition. A positive *Joshi-Effect*, $+\Delta i$, is also obtained when the gas is exposed to potentials near the threshold value. Joshi's oscillographic studies of the phenomenon and subsequent work in these laboratories thereon have shown that the effect is chiefly due to the suppression, on irradiation, of the high frequencies present in the discharge current.

NO_2 was decomposed in the ozonizer at 5 kV (r.m.s.) under two sets of conditions, *viz.*, with the ozonizer (i) in dark and (ii) under irradiation,

It is found that not only the times both for the completion of the change under the discharge and for a certain stage thereof, in the two cases, are sensibly identical but that also the corresponding reaction-time curves are throughout concurrent. This indicates that the high frequency components of the discharge current are not significant for the corresponding chemical effect. This conclusion is in accord with Warburg's view based on a wholly different line of evidence.

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THE RAMAN SPECTRA OF WATER, HEAVY WATER AND ICE

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The Raman spectra of water, heavy water and ice have been studied in detail by a large number of workers though not always with concurrent results. An investigation has been made on their Raman spectra by the present author employing the Rasetti technique of utilising the λ 2536·5 resonance radiation of the mercury arc for exciting the spectra and efficiently filtering off the exciting line from the scattered light by a mercury vapour screen suitably placed. It has been possible from such a study to confirm some of the results reported by earlier workers and also to observe some new features in the Raman spectra of heavy water and ice, which it is proposed to record in this paper.

2. Previous Work

Water.—Adequate summaries of the work done hitherto on the Raman spectrum of water have been given by Magat (1936) and Hibben (1937) and therefore it is not proposed to restate them here. It might, however, be interesting to review here the results reported by the different workers who have used the λ 2537 radiations for excitation of the Raman spectrum of water. Prominent among these are Segre (1931), Holubei (1932), Bolla (1933), Magat (1934), Hibben (1937), Cross, Leighton and Burnham (1937). Nearly all of them agree that the main bands observed in water are at $\Delta\nu = 175$, 500, 700, 1650, 2150, 3200–3650 cm.$^{-1}$ Magat could observe only two bands in the 3200–3650 region, whereas others have noticed three. Bolla has reported that additional bands exist at $\Delta\nu$ 60 and 3990 cm.$^{-1}$ and Holubei has stated that there are many shifts in the region beyond 4000 cm^{-1}. These very high frequency shifts are thought to be improbable by Hibben, who has confirmed the existence of the 175 and 500 cm.$^{-1}$ low frequency bands but not the 700 and 3630 cm.$^{-1}$ Raman shifts. Cross *et al.* also have not noticed Raman lines at about 400 and 700 cm.$^{-1}$

D_2O.—The earliest investigation of the Raman spectrum of heavy water was carried out by Prof. Wood (1934) who used the λ 2537 radiations for excitation of the spectra but not a pure sample of D_2O. He was able to record only a single line at 2517 cm.$^{-1}$ for the liquid and at 2601 cm.$^{-1}$ for the vapour. Rank, Larsen and Bordner (1934), employing the λ 4046 radiation as exciter, observed a line at 2666 cm.$^{-1}$ for D_2O. Magat and Bauer (1935) reported the existence of Raman lines at $\Delta\nu$ 170, 350, 500, 1207, 2389 and 2509 cm.$^{-1}$ Ananthakrishnan (1935) identified $\Delta\nu = 175$, 1110, 1250, 2363, 2515 and 2662 cm.$^{-1}$ in the spectrum of D_2O using λ 4358 as the exciting line. Cross *et al* (*loc. cit.*) noticed a faint band at 1600 cm.$^{-1}$ The low frequency Raman shifts have been attributed to intermolecular oscillations by Magat (1937).

Ice:—Rasetti (1932) was probably the first to study the Raman spectrum of ice using the λ 2537 radiation as exciting source. He observed two lines in the spectrum, one at 53·5 cm.$^{-1}$ and another at 212·1 cm.$^{-1}$ Besides he also noticed a band extending from 3300–3420 cm.$^{-1}$ Rao (1934) was able to record only two bands at 3321 and 3196 cm.$^{-1}$ in the Raman spectrum of ice. Hibben (1937) reported that new frequencies exist in ice at 600, 2225 cm^{-1} also. The Raman spectrum of ice has been studied at $-$ 183° C. by Sutherland (1933) who found a sharp line at 3090 cm^{-1} and a faint companion to it at 3135 cm.$^{-1}$

3. Experimental

The Raman spectra were excited by the λ 2536·5 radiation of a water-cooled magnet-controlled quartz mercury arc of special construction. The general experimental arrangements were the same as described in an earlier paper (Narayanaswamy, 1947). The Wood's tube was also of the same type. A Hilger medium quartz spectrograph having a dispersion of about 140 cm.$^{-1}$ in the λ 2537 region was employed to photograph the spectra. Ilford special rapid plates were usually used. With slit-widths of the order of 0·05 mm. exposures of about 10 hours were given to obtain intense spectra of water and D_2O. For ice, exposures of the order of 4 hours were given. The negatives were measured under a Hilger Cross slide micrometer and microphotometered under a Moll microphotometer.

The water used for this investigation was a chemically pure sample obtained by distillation from $KMnO_4$ and $Ba(OH)_2$ respectively and rendered dustfree by repeated distillation in vacuum. The heavy water was a 99·2 g./100 g. D_2O sample supplied by the Norsk Hydro-Elektrisk Kvaelstofaktieselskab, which was distilled in vacuum. Transparent blocks of ice were used to obtain the Raman spectrum of ice.

Special care was taken to effectively filter out the λ 2536·5 radiation from the scattered light by absorption in a mercury vapour screen suitably placed.

4. Results

Spectrograms showing the salient features of the Raman spectrum of ice, water and heavy water, are reproduced in Figs. 1, 2 and 3 (Plate III) respectively. Microphotometer curves of these spectra are shown in Fig. 5 (Plate III). The positions of the various Raman shifts computed from the negatives and their microphotometer tracings are given in Tables I, II and III for water, D_2O and ice reply. The results of some earlier workers are also given for comparison.

Table I

Raman Shifts observed in Water H_2O in cm.$^{-1}$

	Author		Anantha-krishnan	Magat	Bella	Cross, Leighton and Burnham at (40°)
Exciting line	2537	Int.	4358	2537	2537	2537
Raman lines ..	60	(v. st.)	..	..	60	..
	175	(st.)	134–243	175	172	200
	475	(f.)	464	500	510	..
	758	(ff.)	754	740	780	..
	1630	(m.)	..	1659	1645	1656
	..		..	2135	2150	2167
	3260	(st.)	3214	3200	3200	3190
	3426	(v. st.)	3428	3400	3435	3440
	3610	(m)	3600	..	3630	3650
				5000	3990	4000

Table II

Raman Shifts observed in Heavy Water D_2O in cm.$^{-1}$

	Author		Anantha-krishnan	Magat and Bauer	Cross, Leighton and Burnham
Exciting line	2537	Int.	4358	4558	2537
Raman lines ..	60	(v. st.)	..	..	..
	176	(st)	130–240	170	190
				350	
	300–450	(ff.)	..	~500	..
	..		1110	..	..
	1207	(m.)	1250	1207	1208
	..		..	..	1600
	2373	(st.)	2363	2389	2360
	2539	(v. st.)	2515	2509	2515
	2670	(st.)	2662	..	2680

TABLE III

Raman Shifts observed in Ice in cm.$^{-1}$

	Author		Rasetti	Hibben	Cross, Leighton and Burnham
Exciting line	2537	Int.	2537	2537	2537
Raman lines	52·0	(st.)	53·5	..	..
	213·1	(st.)	212·1	205	210
	210–310 band	(m.)	..		..
	..		..	601	..
	..		..	2225	..
	3147	(v. st.)	3300 band	3136	3150
	3264	(st.)	3420 band	3330	3270
	3347	(st.)			3390

v.st. = very strong; st. = strong; m. = medium; f. = feeble; ff. = very feeble.

Water.—The main band in water is observed in the region 3200–3650 cm.$^{-1}$ Three intensity maxima are discernible in this band at approximately 3260, 3426 and 3610 cm.$^{-1}$ The central component appears to be the most intense one (see Fig. 4, Plate III). No other bands of frequency shift greater than 3610 cm.$^{-1}$ were found in the Raman spectrum of water. With the exposures given, the band at 2150 cm.$^{-1}$ reported by some workers was not observed by the author. The Raman line at 1630 cm.$^{-1}$ is noticed clearly and is of medium intensity.

In the low frequency region, the existence of two very low shifts at 60 and 175 cm.$^{-1}$ has been confirmed. These will be seen clearly in Fig. 2 (Plate III) on the Stokes and anti-Stokes side of the λ 2536·5 line. The bands appear to be very intense. Besides these, two other faint bands are observed with centres at approximately 475 and 758 cm.$^{-1}$ Exposures of longer duration are found to be necessary to obtain these two bands.

Heavy Water.—In the Raman spectrum of heavy water, the main band appears in the shifted position in the region 2300–2700 cm.$^{-1}$ Here also the central component of the band appears to be more intense than the two outer ones. The 1650 water band is observed at 1207 cm.$^{-1}$ in D_2O. In the low frequency region, besides the 175 band which has been observed by earlier workers, a new band at 69 cm.$^{-1}$ is noticed for the first time. These two bands with their anti-Stokes counterparts are easily recognizable in Fig. 3. It is remarkable that the positions of these bands are the same as those of the corresponding bands in water. Their intensities are also of comparable order. There is also a faint band extending from 350–450 cm.$^{-1}$ which was noticed by Magat and Bauer.

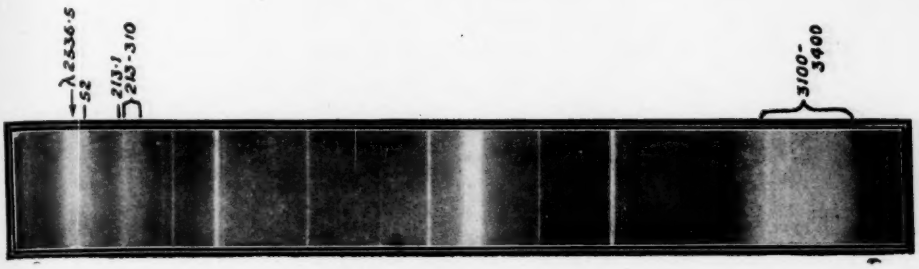

FIG. 1. Raman spectrum of Ice

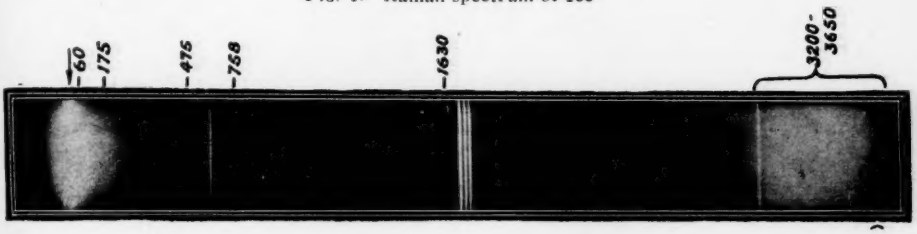

FIG. 2. Raman spectrum of water H_2O

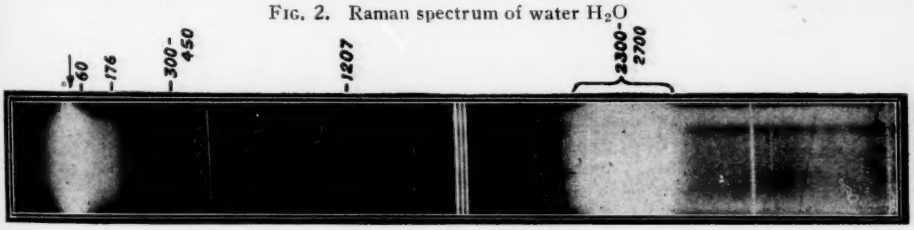

FIG. 3. Raman spectrum of heavy water D_2O

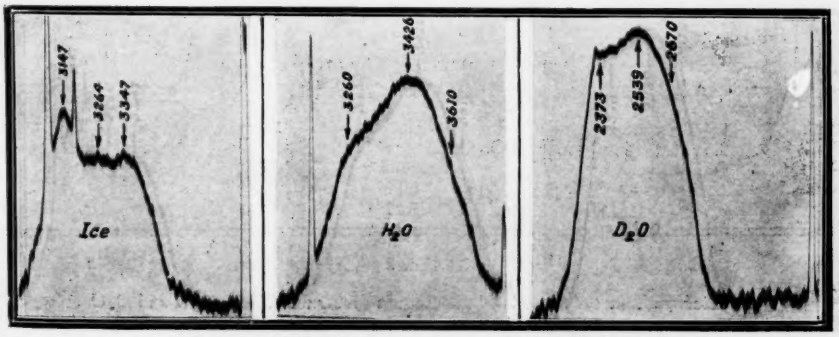

FIG. 4. Microphotometer curves of the main bands

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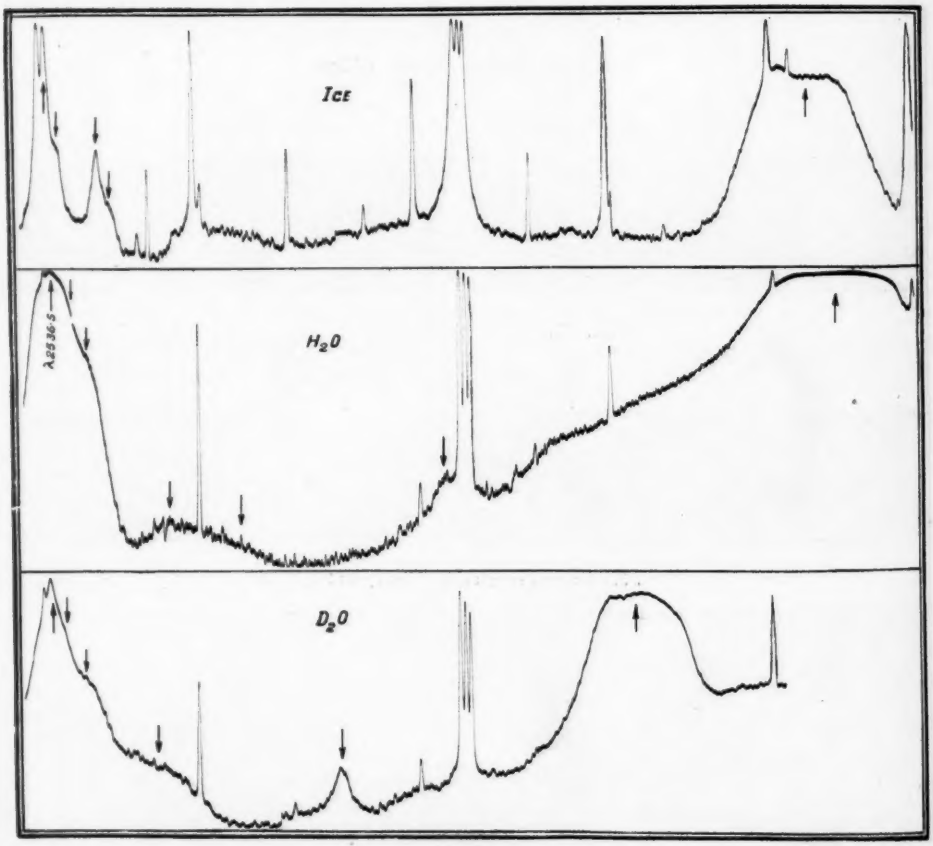

FIG. 5

Microphotometer records of the Raman spectrum of Ice, H_2O and D_2O

Ice.—A Raman line at 53·5 cm.$^{-1}$ reported by Rasetti has been confirmed by the present investigation. A new band has also been observed adjoining the intense 213·1 Raman line. This band extends from 213–310 cm.$^{-1}$ and is reported for the first time. The main band in ice appears better resolved, as may be seen from the microphotometer curve in Fig. 4. The most intense component is the first one at 3147 cm.$^{-1}$ The bands reported by Hibben to occur at 600 and 2225 cm.$^{-1}$ could not be confirmed by the author.

In conclusion, the author wishes to express his gratitude to Professor Sir C. V. Raman, KT., F.R.S., N.L., for his keen interest and guidance in the course of this investigation.

SUMMARY

The Raman spectra of water, heavy water D_2O and ice have been studied using the λ 2537 radiation of the mercury arc as exciter. The shifts observed in water are $\Delta\nu = 60$, 175, 475, 758, 1630, 3260, 3426, and 3610 cm.$^{-1}$ Heavy water exhibits Raman bands at $\Delta\nu = 60$, 176, 300–450, 1207, 2373, 2539 and 2670 cm.$^{-1}$ The band at 60 cm.$^{-1}$ is reported for the first time. A new Raman band is observed in the spectrum of ice extending from 213–310 cm.$^{-1}$, the other Raman lines being at 52, 213·1, 3147, 3264 and 3347 cm.$^{-1}$

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FLUORESCENCE AND PHOSPHORESCENCE OF DIAMOND AT DIFFERENT TEMPERATURES

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1. Introduction

Many diamonds are fluorescent under ultraviolet irradiation and phosphoresce on cutting off the incident light. The fluorescence spectrum of all diamonds at room temperature consists mainly of an electronic line at λ 4156 accompanied by subsidiary vibrational bands on the longer wavelength side and a continuous background (Nayar, 1941). Green fluorescent diamonds exhibit, in addition, an electronic line at λ 5032 accompanied by its vibrational bands and continuum (Mani, 1944). On cooling the diamond to − 180° C., the electronic lines and bands sharpen and shift to shorter wavelengths. Nayar studied also the effect of heating the diamond. With increase of temperature, the line at λ 4156 and its subsidiary bands broaden and shift to longer wavelengths. Ultimately at about 350° C, no trace of the line or bands is noticeable, only a continuous spectrum being present. Naturally, as the line broadens, its apparent intensity diminishes and it becomes diffuse. It is of great interest to find out whether the integrated intensity of the line at λ 4156 changes. The results presented in this paper reveal no appreciable change in the intensity of the line as a whole between − 180° C. and + 150° C., while the results at higher temperatures are inconclusive. In the range − 180° C. to 400° C. the intensity of fluorescence of diamond, viewed through a filter transmitting between λ 4050 and λ 4300, does not markedly change as far as the eye could detect. This fact supports the result mentioned above.

The present opportunity has been taken to continue the studies on the phosphorescence of diamond by the author reported in earlier papers (1946), and some remarkable effects observed have been set forth in this paper.

2. Experimental Technique

For work at liquid-air temperature, the experimental set up for the investigation is the same as that employed by Nayar and Miss Mani (1944). The special demountable Dewar Flask employed by them is used and a

brightly fluorescent (blue) diamond NC 67 is fixed in a copper block by means of Wood's metal and this is screwed on to the bottom of a metal tube which holds the liquid air. The tube is inserted into the pyrex flask and is sealed at the top by means of Apiezon wax, while the flask is evacuated continuously from the bottom by a Cenco pump.

For higher temperature work, a small heater consisting mainly of a rectangular brass tube $1\frac{1}{2}'' \times \frac{1}{2}'' \times \frac{1}{2}''$ is constructed. At the centre of one of the sides of the tube a small opening is made for irradiation purpose. This opening and one of the sides are closed by glass windows. The tube is wrapped up with a thin layer of mica over which is wound nichrome wire and is covered by asbestos. The diamond is stuck on a small copper plate by means of sodium silicate solution and placed at the centre of the heater. The open end is closed by a mica strip through which is inserted a calibrated nichrome-constantan thermocouple for measuring the temperature of the diamond. The diamond is assumed to be at the temperature of the surrounding air. The assumption is a good approximation as diamond is an excellent thermal conductor.

The unfiltered light from a mercury pointolite lamp is focussed on the diamond by a lens and excites fluorescence. The fluorescent light is focussed on the slit of a two-prism Hilger glass spectrograph (E 328) by means of a short focus cylindrical lens. Since the integrated intensity of the electronic line at λ 4156 alone is required, the slit of the spectrograph is kept fairly broad at 20 divisions ($= 0{\cdot}004''$) so that the doublet nature of the line is not revealed at $-$ 180° C. The fluorescence spectra of the diamond at both liquid-air and room temperatures are recorded on a Selochrome plate (D 41) side by side to minimise the errors due to non-uniformity of the plate and identical exposures are given at both temperatures. In one set the exposure is one hour, while in the other it is 2 hours. Similarly a number of spectra at 25°, 60°, 100°, 150°, 200°, 250°, 300°, 350° and 400° C. are taken, the exposure being 23 minutes in each case. During any set of exposures great care is taken to see that the position of the diamond is undisturbed and that all other conditions are identical.

Enlarged microphotometer curves of the electronic line using the gear ratio of 1 : 50 for the recording drum is obtained for each of the four spectra of the first plate. For spectra at higher temperatures microphotometer curves of a large region around the electronic line is recorded using the normal gear ratio of 1 : 7.

Using the well-known method of graded intensity marks the density-intensity curve of a Selochrome plate—from the same packet as that used

for recording the fluorescence spectra—is obtained. The density of blackening of the electronic line at various distances from its centre is deduced from the microphotometer records and the corresponding intensity distribution curve in each case is plotted, using the density-intensity curve of the plate.

3. Results

Photographs of fluorescence spectra of diamond kept at 25° and — 180° C. are reproduced in Fig. 1, Plate IV. Fig. 2 shows spectra with the diam ond at 25°, 60°, 100°, 150°, 200°, 250°, 300° 350° and 400° C. These pictures reveal the shifting and broadening of the electronic line at λ 4156 with increasing temperature. The diminution in peak intensity is also seen clearly. In addition the intensity of the continuous spectrum diminishes.

As the electronic line is symmetrical at liquid air and room temperatures, the area enclosed by the intensity distribution curve between the two ordinates at half intensity gives a measure of the integrated intensity of the electronic line. This is found to be appreciably constant at the two temperatures within limits of experimental error.

On the other hand at high temperatures, the line is apparently unsymmetrical due to decrease in peak intensity and broadening and consequent large overlapping of the continuous spectrum. The effect due to this is eliminated by extrapolating the curve of the continuous spectrum at large distance from the centre of the electronic line and subtracting this intensity from the original intensity distribution curve. The resulting curve for the electronic line is considerably more symmetrical. Even in this curve, only the integrated intensity over half width on the shorter wavelength side is calculated. This is found also to be appreciably unaltered for the temperatures between 25° C. and 150° C. At higher temperatures it is difficult to distinguish the peak of the electronic line from the background. But it seems fairly probable that the broadening accounts for the diminution in the peak intensity of the line even at higher temperatures and that the intensity of the electronic line as a whole does not change in any marked manner. As far as the continuous spectrum is concerned, the author is of the opinion that it decreases to some extent with temperature but does not vanish even at 400° C. Tables I and II give the results obtained.

The ratios in the last column are very nearly equal to one, allowing for experimental errors. The microphotometer curves of a few mercury lines scattered by the diamond showed that the intensity of the source did not vary by more than one per cent. during the course of the investigation.

TABLE I

Temperature	Exposure	Integrated Intensity of λ 4156	Ratio of the integrated intensities
25° C.	60 min.	138·9	1·05
−180° C.	60 min.	146·2	
25° C.	120 min.	242·0	0·99
−180° C.	120 min.	239·3	

TABLE II

Temperature	Exposure	Integrated Intensity of λ 4156	Ratio of the Integrated intensities
25° C.	23 min.	8·48	0·96
150° C.	23 min.	8·17	

Hence, no correction for this factor is necessary. As two spectral lines to be compared have nearly the same frequency and as they are in juxtaposition on the plate, most of the errors due to non-uniformity of the plates and of development are almost entirely eliminated. Finally the accuracy of the experimental results can be verified as follows:—

The ratio of the integrated intensities for the two exposures at room temperature given in Table I is 1·74. According to the well-known Schwarschild's relation this value is to be expected as the effect of doubling the exposure time is equivalent to increasing the intensity by $2^{0.86}$ (= 1·81).

4. PHOSPHORESCENCE OF DIAMOND

For making visual observations on the fluorescence and phosphorescence of diamond at various temperatures, sunlight passed through a Wood's glass filter is used for exciting fluorescence. The extremely bright fluorescence of the diamond NC 67, blue in colour, does not show any great change in intensity or colour between − 180° C. and + 400° C. On the contrary, the after-glow on shutting off the incident light is very feeble and greenish-yellow at low temperatures. At 150° C. the colour changes to blue and the glow is brighter and lasts a longer time. At 400° C., the glow is extremely bright and blue. On shutting off the incident light no discontinuity between the brightness of fluorescence and of phosphorescence is observed. The bright and blue glow slowly decays starting with an initial intensity nearly as bright as that of fluorescence. Even at 400° C., surprisingly enough in order to build up this great store of energy released as

after-glow, it is necessary to expose the diamond only for less than a fraction of a second to the exciting radiation.

The slow decaying bright and blue glow can be quenched by irradiating the diamond with intense red or green light for a few seconds. Also if full sunlight without any filter is used for exposing the diamond a flash of blue after-glow can be seen for a second or two and it turns to a comparatively feeble and greenish-yellow glow lasting only for a few seconds. These results are similar to the quenching effect by light or heat on the stored-up energy of diamond at room tempeature.

Again, the after-glow is blue when ultra-violet or violet light is used for irradiating the diamond. On the other hand, with green light (λ 5000 to λ 6000) as the exciting source, the glow is distinctly greenish-yellow and very weak comparatively. With red light no perceptible glow can be detected. All these results are in agreement with the Stokes Law of fluorescence.

In conclusion the author wishes to thank Sir C. V. Raman, KT., F.R.S., N.L., for his constant interest in this problem suggested by him.

SUMMARY

The electronic line at λ 4156 present in the fluorescence spectrum of all diamonds sharpens and increases in peak intensity on cooling the diamond; *per contra*, it broadens and decreases in peak intensity on increasing the temperature of the diamond and finally at 350° C. is lost in the background. The integrated intensity of the line has been investigated and found to be unaltered to any marked degree between $-$ 180° C. and $+$ 150° C.

The phosphorescence of diamond at various temperatures has also been dealt with. At low temperatures the after-glow is weak and greenish-yellow in colour, while at 400° C., the glow is extremely intense and blue. The effect of quenching by red or green light on this bright and blue glow has been reported in this paper.

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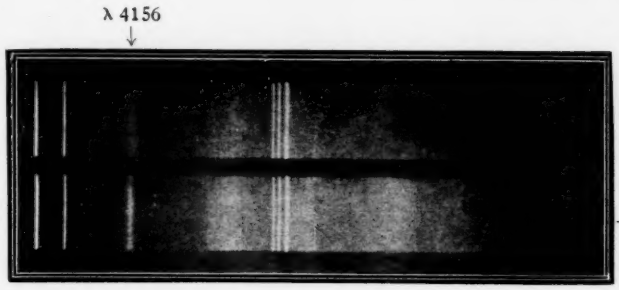

FIG. 1

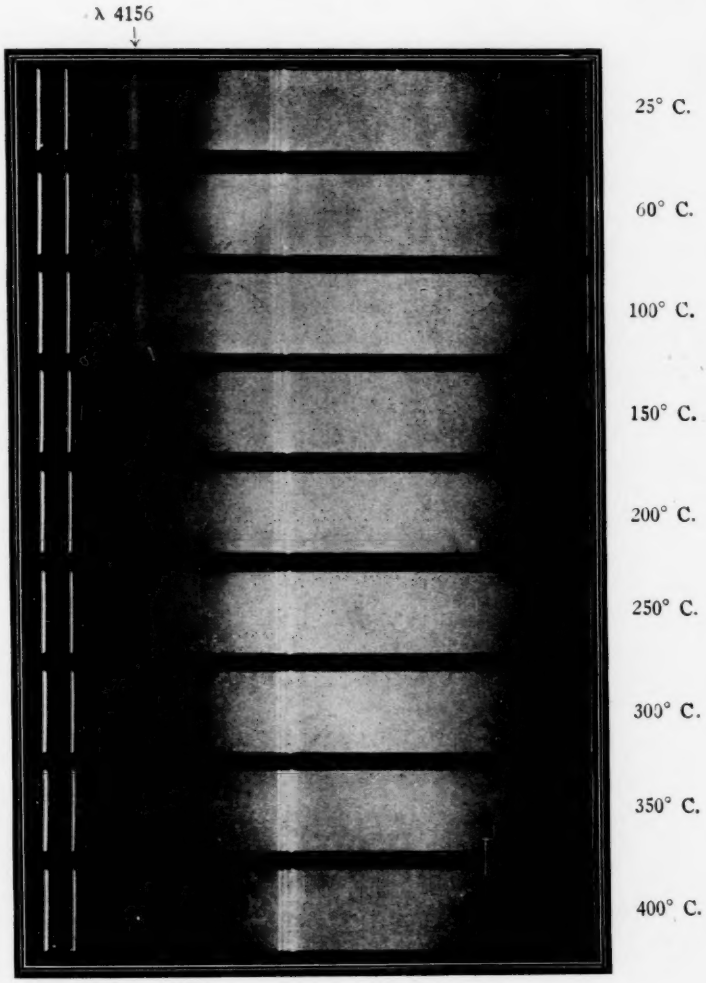

FIG. 2
Fluorescence Spectra of Diamond at Different Temperatures

RAMAN SPECTRUM OF AMMONIUM BROMIDE AND ITS VARIATION WITH TEMPERATURE

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1. Introduction

As was pointed out in a recent paper which appeared in these *Proceedings* (Krishnan, 1947) a study of the effect of temperature on the Raman spectra of ammonium halides offers a means of settling two fundamental issues connected with these solids, namely (1) the behaviour of the NH_4 ions in the neighbourhood of the transition temperature and (2) the nature of the lattice spectrum in which the NH_4 ions oscillate as single units. Accordingly, the author undertook a thorough investigation of the Raman effect in ammonium halides in the form of single crystals and its variation with temperature using the λ 2536·5 mercury resonance radiation as exciter. The results obtained with ammonium chloride which have already been reported in the paper referred to above, indicated that Pauling's hypothesis that there was onset of free rotation of the NH_4 ions immediately above the transition temperature was not correct. They also confirmed the discrete character of the vibration spectrum of the ammonium chloride structure (which is of the cæsium chloride type), as demanded by the new crystal dynamics. These investigations have now been extended to the case of ammonium bromide and the results are presented in this paper.

2. Earlier Work

Studies on the Raman effect in crystalline ammonium bromide are very scanty. Its spectrum was first photographed by Kastler (1932) who reported the existence of three lines with frequency shifts 2810, 3030 and 3130 cm.$^{-1}$ Subsequently, Menzies and Mills (1935) identified five Raman lines with frequency shifts, 1380, 1420, 1689, 3032 and 3140 cm.$^{-1}$ in the spectrum of ammonium bromide taken at room temperature. They further investigated the effect of temperature on the Raman spectrum in the range from 25° C. to − 150° C. With decrease of temperature of the crystal, the spectrum sharpened considerably, while there was no change in the relative intensities of the lines. Unlike in the case of ammonium chloride, Menzies and Mills failed to observe any low frequency Raman lines in the spectrum of ammonium bromide taken below the transition temperature, *i.e.*, 235° T. (− 38° C).

Using the technique of complementary filters for crystal powders, Anantakrishnan (1937) photographed the Raman spectrum of ammonium bromide. Besides confirming the results obtained by Menzies and Mills, Anantakrishnan reported the existence of two additional Raman lines with frequency shifts 2000 and 2800 cm.$^{-1}$

None of the investigators mentioned above has recorded any low frequency line in the Raman spectrum of ammonium bromide. Even as regards the internal frequencies of oscillation of the NH_4 ion, their studies appear to be far from being complete. This fact may be attributed to the use by the earlier workers of the λ 4046 and λ 4358 radiations of the mercury arc as exciter. Ammonium bromide being transparent to the ultra-violet, the λ 2536·5 mercury resonance radiation could be profitably used to obtain more satisfactory spectrograms.

3. Details of the Experiment

Transparent crystals of ammonium bromide were prepared by the method of slow evaporation from aqueous solutions of the salt. In order to facilitate the growth of crystals in the form of cubes a small quantity of urea was added to the solution. The largest single crystal grown by this method had the dimensions of $1 \times 1 \times 0 \cdot 5$ cm. The specimens were slightly coloured yellow.

The experimental technique employed by the author for photographing the Raman spectrum at different temperatures has already been described in one of the earlier papers (Krishnan, 1947). Using the Hilger E 3 quartz spectrograph, photographs of the Raman spectrum of ammonium bromide were taken with the crystal maintained successively at 85° T., 173° T., 308° T. and 398° T. Exposures of the order of twelve hours were given for the low temperature photographs, as the optical arrangement was not very efficient due to the necessity for the use of windows for the demountable Dewar flask. Four hours were sufficient to get reasonably intense spectrograms at room temperature. At 398° T., the crystal became translucent and consequently satisfactory photographs could not be taken at this temperature.

4. Results

Photographs of the Raman spectrum of ammonium bromide taken at 308° T., 173° T. and 85° T. are reproduced in Figs. 1 to 3. The corresponding microphotometer records are also included in the Figures. In Fig. 4 are reproduced photographs of the Raman spectrum of ammonium bromide taken at four different temperatures together with two photographs of the Raman spectrum of ammonium chloride taken at room temperature and

at liquid-air temperature. The positions of the Raman lines together with their frequency shifts in wave-numbers from the exciting line are marked in Figs. 1 to 3. The most striking feature of the Raman spectrum of ammonium bromide which has not been noticed before is the appearance of a lattice spectrum consisting of a series of sharply defined lines with frequency shifts varying from about 50 cm.$^{-1}$ to about 600 cm.$^{-1}$ In the high frequency shift region also, the photographs taken by the author exhibit many more Raman lines than those reported by the earlier workers. The Raman shifts of ammonium bromide are classified under two heads, namely (1) low frequency or lattice spectrum and (2) the spectrum of the NH_4 group.

The lattice spectrum.—Microphotometer records of the lattice spectrum of ammonium bromide taken at different temperatures are reproduced in Fig. 5. The frequency shifts of the lattice lines together with visual estimates (figures given in brackets) of the relative intensities of the lines are entered in Table I.

TABLE I

Lattice spectrum of crystalline NH_4Br

Sl. No.	Group	85° T.	173° T.	308° T.	398° T.
1	I	69 (15)	63 (15)	56 (12)	51 (12)
2		77 (6)	75 (8)	75 (3)	70 (4)
3		136 (10)	133 (8)	128 (6)	124 (5)
				136 (6)	134 (5)
4		158 (0)	156 (2)	155 (4)	150 (5)
5		182 (12)	178 (8)	175 (2)	171 (2)
6	II	260 (1)	258 (2)	256 (1)	
7		315 (1)			
8		335 (5)	328 (3)	325 (0)	
9	III	490 (3)	490 (1)	450 (1)	
10		626 (4)			
11		660 (2)			

The spectrum consists of a series of discrete frequency shifts of which the one nearest to the exciting line is the most intense. At liquid-air temperature (*i.e.*, 85° T.) the lines are extremely sharp. As the temperature of the crystal is slowly raised, the lines become less sharp and exhibit progressive shift in their positions. The discrete character of the spectrum persists even at 398° T., *i.e.*, about 163 degrees above the transition temperature. See the microphotometer records reproduced in Fig. 5 (*d*). At this temperature some of the lines especially those lying in the region of frequency shifts 100–200 cm.$^{-1}$ are so broad that they run into one another. It should be remarked that unlike in the case of ammonium chloride, the lattice

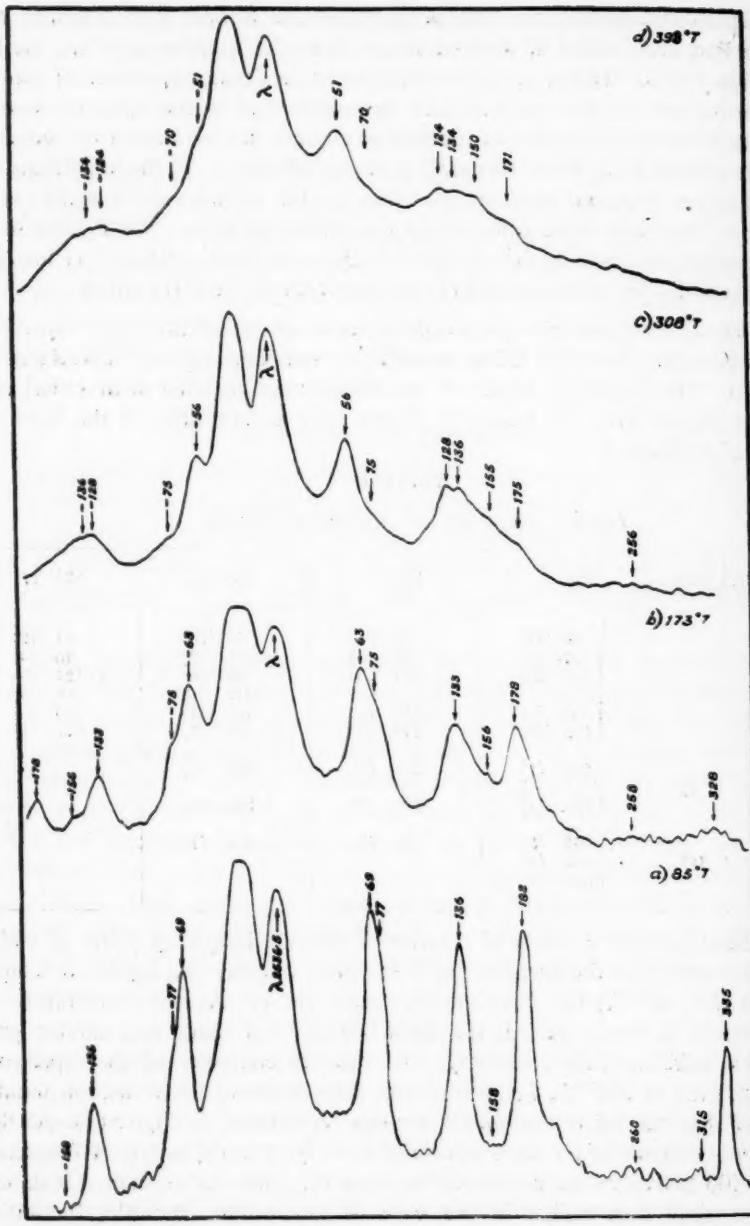

FIG. 5. Microphotometer records of the lattice spectrum of ammonium bromide taken at different temperatures.

spectrum of ammonium bromide does not exhibit any striking change in its structure when the temperature of the crystal is lowered from room temperature to that of liquid air.

At liquid-air temperature the lattice spectrum consists of eleven lines. They can be classified under three groups depending on their frequency shifts. The first group comprises of the lines falling in the region of frequency shifts 0–200 cm.$^{-1}$, the 2nd those falling in the region 200–400 cm.$^{-1}$ and the 3rd those falling in the region 400–700 cm.$^{-1}$ The first group contains the most prominent lines. In the spectrum taken at 85° T., the line with the frequency shift 77 cm.$^{-1}$ falls very close to the intense line at 69 cm.$^{-1}$ Nevertheless, it can be seen clearly resolved from the latter on the anti-Stokes side of the photograph (Fig. 3 *c*) or in the microphotometer record reproduced in Fig. 5 (*a*). The lines with frequency shifts 620 and 660 cm.$^{-1}$ coming under the third group fall adjacent to the mercury lines λ 2576·3 and λ 2578·4 respectively. They are, however, easily discernible in the photograph reproduced in Fig. 3 (*c*).

As the temperature of the crystal is raised, the general intensity of the lines coming under the first group undergoes very little change. The 2nd, 3rd and 5th lattice lines progressively decrease in intensity, while the 4th line increases in intensity. At 308° T. and above, the 3rd line is split up into components. The proportionate shift with variation of temperature is different for different lines.

The three lattice lines falling in the second group become progressively weaker in intensity with increase of temperature. At 85° T. the third line with a frequency shift of 335 cm.$^{-1}$ is sharp and fairly intense. When the temperature is raised to 173° T. this line shows an abrupt fall in intensity. See Figs. 5 (*a*) and (*b*). The spectrum taken at 398° T. exhibits a feeble continuum extending from about 200 to 400 cm.$^{-1}$ and exhibiting some structure. The intensity of the continuum decreases with increasing frequency shift. In the spectrograms taken at 173° T. and above, no lines are recorded corresponding to the 626 and 660 lines observed at 85° T.

The spectrum of the NH_4 ion.—The lines with frequency shifts greater than 1390 cm.$^{-1}$ appearing in the Raman spectrum of ammonium bromide are catalogued in Table II. Visual estimates of the relative peak intensities have been made and the values are given in brackets. The frequency shifts of the Raman lines of ammonium bromide recorded earlier by Menzies and Mills (1935) at 123° T. and those obtained by them and by Ananthakrishnan (1937) for room temperature are also entered in Table II.

TABLE II

Raman lines due to internal oscillations in NH_4Br

Group	Low Temperature			Room Temperature		
	Menzies and Mills 123° T.	Krishnan 85° T.	Krishnan 173°	Krishnan	Menzies and Mills	Anantha-krishnan
IV		1401 (3s)	1399 (2s)	1398 (4s)	1380	1395
		1420 (2s)	1416 (1s)			
	1456	1435 (1s)	1432 (1s)	1429 (2s)	1420	
VIII		1491 (2s)	1480 (1s)	1472 (1b)		
II	1694	1693 (20s)	1690 (20s)	1686 (25s)	1689	1690
VIII		1979 (6s)	1976 (5b)	1960 (3bd)		2000
		1986 (6s)				
V		2794 (1s)				
		2816 (10s)	2814 (10b)	2806 (8b)		2800
		2836 (6s)				
		2886 (1s)	2885 (1)			
		2970 (5b)	2987 (6b)			
I	3035	3038 (30s)	3037 (30s)	3037 (30b)	3032	3025
		3080 (10s)	3078 (8s)			
III	3118	3122 (25s)	3122 (25s)	3121 (25b)	3140	3126
VI		3202 (8s)	3208 (10b)	3211 (10b)		
		3254 (5s)				
		3289 (6s)	3276 (6b)	3267 (8b)		
		3306 (4s)				
		3346 (4s)	3338 (4s)	3323 (5)		
		3392 (1s)		3368 (4)		
		3470 (1b)	3454 (1b)	3450 (1)		

The spectrum at room temperature exhibits no less than 13 Raman shifts as against six reported by Ananthakrishnan. The lines are of varying width. At 173° T., 16 Raman lines have been identified, whereas at 85° T. no less than 22 Raman lines could be seen as against 4 reported by Menzies and Mills. See Figs. 2 and 3. The observed Raman frequencies have been classified under eight groups as shown in Table II. In the spectrum taken at room temperature the Raman lines are in general broad and diffuse. The line at ~ 1960 cm.$^{-1}$ has the maximum width which is of the order of 60 cm.$^{-1}$ As the crystal is cooled down, the lines sharpen considerably. Besides, some lines split up into components. This is particularly noticeable in the case of the lines ~ 1960 and ~ 2806 cm.$^{-1}$ These changes appear to take place gradually and not abruptly very near the so-called λ-point transition (235° T.).

5. Discussion

Before discussing the significance of the results described in the last section, it is useful to recall some of the known properties of ammonium bromide and their variations as one passes through the transition temperature. X-Ray studies carried out by Bartlett and Langmuir (1921), Ketelaar (1934) and by Weigle and Saini (1936) indicate that ammonium bromide exists in three modifications. The α-NH_4Br which is stable above 138° C. possesses the sodium chloride structure (face-centred cube). The β-NH_4Br which is stable between — 40° C. and 138° C. has the cæsium chloride structure (body-centred cube); each nitrogen atom is surrounded by 4 hydrogen atoms tetrahedrally and by 8 chlorine atoms at the corners of a cube. Below — 40° C. the cubic form undergoes slight deformation into the tetragonal form, γ-NH_4Br. Ketelaar observed extra X-ray reflections with NH_4Br at — 100° C. They reveal the occurrence of a superlattice in the crystal structure of the low temperature modification. From this Ketelaar concluded that γ-NH_4Br belongs to the space group D^7_{4h}, each unit cell containing two molecules of NH_4Br. According to Weigle and Saini, the change from the cubic to the tetragonal form may be regarded as a contraction by two of the cubic axes by 3 parts in 1000 and by 2% displacement by the bromine ions along a 3rd axis in alternatively a positive and negative direction with respect to the two shortened axes. This result fits in with the observation made by Simon and Bergmann (1930) on the thermal expansion of ammonium bromide. The coefficient of thermal expansion assumes a negative value just at the transition temperature, while above and below the transition temperature it has a positive value. This observation of Simon and Bergmann has been confirmed by Weigle by the X-ray method. Ruhemann (1927) measured the specific heat of ammonium bromide above and below the transition temperature. While passing through the transition temperature the specific heat at constant pressure increases rapidly and falls again to the normal value. Unlike cold ammonium chloride, ammonium bromide is not piezo-electric both above and below the transition temperature (Hettich and Schleede, 1928). According to the observations of Hettich (1934), ammonium bromide exhibits double refraction below the transition temperature showing thereby that its crystal structure does not possess cubic symmetry. As it is also non piezo-electric, the correct space group of the cold bromide should be D^7_{4h}.

As in the case of ammonium chloride, the anomalous behaviour of ammonium bromide near the transition temperature has been attributed by Pauling (1930) to the existence of free rotation of the NH_4 ion in the lattice above the transition temperature. Frenkel (1935), on the other hand,

favoured the view that both above and below the transition temperature, the NH_4 ion executes rotational oscillations the only difference being that above the transition temperature the orientations are irregularly distributed. The appearance of a lattice spectrum with discrete frequency shifts and with great intensity in crystalline ammonium bromide at temperatures far above the transition point as revealed by the present study does not support Pauling's hypothesis. If the NH_4 ion is capable of free rotation above the transition temperature as suggested by Pauling, and in consequence possesses spherical symmetry, none of the atomic vibrations in which NH_4 moves as a unit should appear as fundamentals in the Raman effect due to the similarity of its structure to that of cæsium chloride. The very appearance of a lattice spectrum with discrete frequency shifts at ordinary temperatures and its persistence without any striking change below the transition temperature support Frenkel's explanation, namely, that both above and below the transition temperature the NH_4 ion executes rotational oscillations and that only a reorientation of the NH_4 tetrahedra takes place in the lattice at the transition temperature.

The activity of the lattice vibrations of ammonium bromide in the first order Raman effect enables one to observe directly the discrete nature of the vibration spectrum of the cæsium chloride type of structure and thus to confirm the validity of Raman dynamics. K. G. Ramanathan (1947) has given expressions for the frequencies of the fundamental modes of oscillation of the cæsium chloride structure. The respective modes and the formulæ for the frequencies are enumerated in Table III. With the help of these formulæ, it is possible to give tentative assignments to the lattice lines appearing in the spectrum of ammonium bromide taken above the transition temperature. In order to do this, it is necessary to know whether all the observed low frequency lines given in Table I belong to the first order spectrum or not. In the case of NH_4Cl the first order lattice spectrum is confined to a region of frequency shifts, 0–200 cm.$^{-1}$ It follows therefore that the first order lattice spectrum of NH_4Br should not extend beyond 200 cm.$^{-1}$ On this basis, one can assign the lattice lines coming under Group I (see Table I) to the first order spectrum while those coming under Group II to the second order spectrum.

To a first approximation, the eleven modes of oscillation characteristic of the cæsium chloride structure have only seven distinct frequencies, ν_1 to ν_7 as given in Table III. Of these, ν_7 should be very weak. The six lattice lines appearing in the spectrum taken at 308° T. may be identified with ν_1 to ν_6. The corresponding frequency shifts are entered in column 7 of Table III. Because of the high refractivity and the heavy mass of the

TABLE III

Vibration spectrum of the NH_4Br lattice above the transition temperature

TABLE III

Vibration spectrum of the NH_4Br lattice above the transition temperature

Sl. No.	Oscillating planes	Nature and direction of oscillation	Degeneracy	Formula $4\pi^2\nu^2c^2$		Frequency in cm.$^{-1}$ observed at 308° C.
I	Dodecahedral	NH_4, Br in phase ; normally along [1$\bar{1}$0] NH_4, Br out of phase : tangentially [110]	6	$\frac{P-2T}{m_1}+\frac{P'-2T'}{m_2}+\frac{4(T+T')}{m_1+m_2}$	ν_1	175
II	Two Lattices	NH_4 against Br, arbitrary	3	$\frac{P+2T}{m_1}+\frac{P'+2T}{m_2}$	ν_2	136
III	Cubic	NH_4 alone oscillating normally along [100]	3	$\frac{P-2T}{m_1}$	ν_3	155
IV	Octahedral	NH_4 alone oscillating along any three orthogonal directions	3	$\frac{P-2T}{m_1}$		
V	Cubic	NH_4 al one oscillating tangentially along [010] or [001]	6	$\frac{P+2T}{m_1}$	ν_4	128
VI	Dodecahedral	NH_4 tangentially along [100] contained in the [110] plane	3	$\frac{P+2T}{m_1}$		
VII	Cubic	Br alone oscillating along [100] normally	3	$\frac{P'-2T'}{m_2}$	ν_5	75
VIII	Octahedral	Br alone osscillating in any three orthogonal directions	3	$\frac{P'-2T'}{m_2}$		
IX	Cubic	Br alone oscillating tangentially along [010] or [001]	6	$\frac{P'+2T'}{m_2}$	ν_6	56
X	Dodecahedral	Br tangentially along [100] contained in the [110] plane	3	$\frac{P'+2T'}{m_2}$		
XI	Dodecahedral	NH_4 Br in phase, tangentially along [110] NH_4 Br out of phase ; normally along [110]	6	$-\frac{4(T+T')}{m_1+m_2}$	ν_7	

P and *P'* represent the force on any atom proportional to its own displacement and *T* and *T'* represent the force on any atom proportional to the displacement of the next nearest neighbours. The undashed quantities refer to the NH_4 ion and the dashed ones to Br ion. m_1 and m_2 are the respective masses of NH_4 and Br ions.

bromine ions, those oscillations in which the bromine ions alone move may be expected to appear with great intensity and should have the lowest frequencies. The most intense line at 56 cm.$^{-1}$ is therefore assigned to ν_6 and the next line at 75 cm.$^{-1}$ to ν_5. Since P $\approx$ P′, and T $\approx$ T′, ν_3/ν_5 and ν_4/ν_6 should be nearly equal to $\sqrt{\frac{m_2}{m_1}}$. The pairs of lines 56–128 cm.$^{-1}$ and 75–155 cm.$^{-1}$ satisfy the above relationship. Therefore, the lines 128 cm.$^{-1}$ and 155 cm.$^{-1}$ have been assigned respectively to ν_4 and ν_3. The remaining two lines 175 and 136 have been assigned to ν_1 and ν_2 respectively as they roughly satisfy the relationships:—$\nu_1^2 \approx \nu_3^2 + \nu_5^2$ and $\nu_2^2 \approx \nu_4^2 + \nu_6^2$. At 308° T. the lattice lines are rather broad and most of them run into one another. The frequency shifts given in Table I correspond to the positions of maxima as judged from the microphotometer record (Fig. 5 *c*). In view of this, no attempt has been made to evaluate the force constants P, P′, T and T′ from the observed frequencies.

Below the transition temperature, the crystal structure belongs to the tetragonal class. The expressions for the frequencies of oscillations for this type of structure have not been worked out on the basis of the new crystal dynamics. Therefore no quantitative comparison of the experimental results with theory is possible at present; but certain features of the spectrum may be mentioned. At 173° T., the first order lattice spectrum exhibits 5 lines. The frequency shifts of the 1st and 2nd lines are related to the shifts of the 3rd and 4th lines in the inverse ratio of the square roots of the masses of bromine and ammonium ions. It follows therefore that the first two lines arise from the oscillations of the bromine ions alone, while the next two lines are due to the oscillations of the NH_4 ions.

The Spectrum of the NH_4 ion.—The observed frequency shifts in crystalline ammonium bromide lying in the neighbourhood of 3000, 1700, 3100 and 1400 and classified under Groups I, II, III and IV in Table II, represent the fundamental frequencies of internal oscillation of the NH_4 ion. In the crystalline state, the degeneracies of the four characteristic frequencies of the free NH_4 ion appear to have been partly removed as indicated in Table IV.

The corresponding frequency shifts observed in the spectrum of NH_4Cl are also included in Table IV for purposes of comparison. In crystalline NH_4Br, only the degeneracy of ν_4 is removed, whereas corresponding to ν_2 and ν_3 of the free ion, only single lines are recorded both at 308° T. and at 85° T. In the case of NH_4Cl, on the other hand, the degeneracies of ν_2, ν_3 and ν_4 are completely removed at 85° T. It follows therefore that

TABLE IV

Raman frequencies of the NH_4 ion

State		ν_1 (1)	ν_2 (2)	ν_3 (3)	ν_4 (3)
Free ..	ion	3033	1685	3134	1397
NH_4Br Crystal	308° T.	3037	1686	3121	1398, 1429
	85° T.	3038	1693	3122	1401, 1420, 1435
NH_4Cl crystal	308°T.	3041	1710, 1765	3146	1400, 1418, 1440
	85° T.	3048	1716, 1790	3121, 3138, 3162	1401, 1420 ?

(Figures given in brackets represent the respective degeneracies.)

the force fields surrounding the vibrating NH_4 ion are more symmetrical in crystalline NH_4Br than in crystalline NH_4Cl. This is true both at room temperature and at the temperature of liquid air.

In the photographs taken at 173° T. and 85° T, the most intense line corresponding to the totally symmetric oscillation of the NH_4 ion has a weak companion at about 3080 cm.$^{-1}$ This may be assigned as a combinational line ($\nu_2 + \nu_4$) which appears with some appreciable intensity due to its proximity to the most intense line at $\backsimeq$ 3038 cm.$^{-1}$ See Table IV.

As in the case of ammonium chloride, the spectrograms taken with ammonium bromide exhibit four groups of bands (V, VI, VII and VIII of Table II) with frequency shifts lying in the neighbourhood of 2800, 3200–3470, 1980 and 1490 cm.$^{-1}$, some of which are fairly intense. They have been observed for the first time. Table V gives the frequency shifts of the groups of extra bands observed in the Raman spectra of ammonium chloride and bromide. The frequency shifts of the intense bands are shown in heavy type. There is complete correspondence between the bands appearing in the bromide spectrum and those appearing in the chloride spectrum except for the following. The frequency shifts in the case of the bromide are generally less than those in the chloride. The bands in the chloride are broader than the corresponding ones in the bromide. The chloride exhibits an intense band at $\backsimeq$ 1800 cm.$^{-1}$, whereas there is no such band in the bromide spectrum. The latter shows a weak line at about 1490 cm.$^{-1}$ which is absent in the chloride spectrum. The significance of these results will be discussed in a later paper.

TABLE V

	Liquid air temperature		Room temperature	
	NH_4Cl	NH_4Br	NH_4Cl	NH_4Br
VIII	**1810**	1491	1780	1462
VII	**2025**	1979	2010	1960
	2025	1986		
V		2794		
	2829	**2816**	2828	2806
		2836		
	2876	2886		
		2970		
VI	**3215**	**3202**		
	3235	3254	**3231**	**3211**
	3285	**3289**		
	3310	3306	3308	**3267**
	3365	3346		
	3395	3392	3380	3323
	3420			
	3515	3470		3450
	3535		3518	

6. INFRA-RED SPECTRUM

The absorption and reflection spectra of crystalline ammonium bromide in the infra-red region were examined by Reinkober (1921) who recorded five maxima corresponding to some of the frequencies of oscillation of the NH_4 ions in the crystal. Pohlmann (1932) made a detailed investigation of the infra-red absorption spectrum of thin layers of ammonium bromide at room temperature and at $-$ 80° C. (193° T.). From the absorption curves reproduced in his paper, the author was able to identify 20 maxima for the room temperature and 23 maxima for $-$ 80° C. The frequency shifts corresponding to these maxima have been evaluated and entered in Table VI. Those given in heavy types correspond to positions of intense absorption. The Raman shifts recorded in the spectra of ammonium bromide taken at 308° T. and 173° T. are also given in the same table. The internal oscillations of the NH_4 ion are active both in Raman effect and in infra-red absorption.

Beck (1944) has investigated the fine structure of the infra-red absorption band of ammonium bromide lying in the region 5–6 μ at four different temperatures, namely 27° C., $-$ 20° C., $-$ 45° C. and $-$ 60° C. He recorded eleven peaks in the region 1602–1750 cm.$^{-1}$ with an average separation of

TABLE VI

Raman and infra-red frequencies characteristic of the NH_4 ion in NH_4Br

Low Temperature		Room Temperature	
Raman 173° T.	Infra-red 193° T.	Raman	Infra-red
	1359		1360
1399	1382		1389
1416	1417		1374
1432	1443	1398	1410
	1467	1429	1437
1480	1483	1462	1468
	1648		1483
	1662	1686	1680
	1673		1697
1690	1698		1717
	1740		1728
1976			1739
2814	2830		1757
2885			1768
2987	2963	1960	
	2990	2806	2830
3037	3009	3037	3055
3076	3060	3121	3162
3122	3150	3211	
3208	3202	3267	
	3240	3323	3313
3276	3271	3368	3362
3338	3305	3450	3460
	3372		
3454	3486		

14·8 cm.$^{-1}$ between two consecutive peaks. The fine structure appeared practically unaltered at 27° C. and — 20° C. Between — 20° C. and — 45° C. there was a noticeable change in the fine structure which persisted down to at least — 60° C. The fine structure appeared at the same wavelengths but with decreased intensity at lower temperatures. The absorption curve for the bromide showed more irregularity than that for the chloride. The appearance of the fine structure below the transition temperature should be attributed to the torsional oscillations of the NH_4 ions.

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7. SUMMARY

Using the λ 2536·5 mercury resonance radiation as exciter, the Raman spectrum of crystalline ammonium bromide has been photographed with the crystal maintained successively at four different temperatures, namely, 398°, 308°, 173° and 85° T. The following facts emerge from this study:—

(1) In the region of temperatures investigated, the Raman spectrum of ammonium bromide exhibits a series of low frequency or lattice lines a fact which has been noticed for the first time. The frequency shifts, intensities and widths of the lines are found to vary with temperature. The lines observed in the spectrum taken above the transition temperature (235° T.) have been identified as the fundamental modes of vibration of the cæsium chloride structure in which the NH_4 ions oscillate as units as demanded by the new crystal dynamics.

(2) The lattice spectrum exhibits discrete frequency shifts even at 398° T., *i.e.*, 163° above the transition temperature. This does not support Pauling's hypothesis that there is onset of free rotation of the NH_4 ions above the transition temperature.

(3) The spectrum characteristic of the NH_4 ions exhibits 5 distinct Raman lines at room temperature and 6 lines at liquid-air temperature. From this it is concluded that the oscillating NH_4 ions do not possess the full tetrahedral symmetry. A comparison of the spectrum of NH_4Br with that of NH_4Cl reveals that the oscillating NH_4 ions in NH_4Br possess a higher order of symmetry than those in NH_4Cl.

(4) The spectra recorded at all temperatures reveal the presence of a large number of bands of which those lying in the region $\simeq$ 2800 and 3200–3500 are the most prominent.

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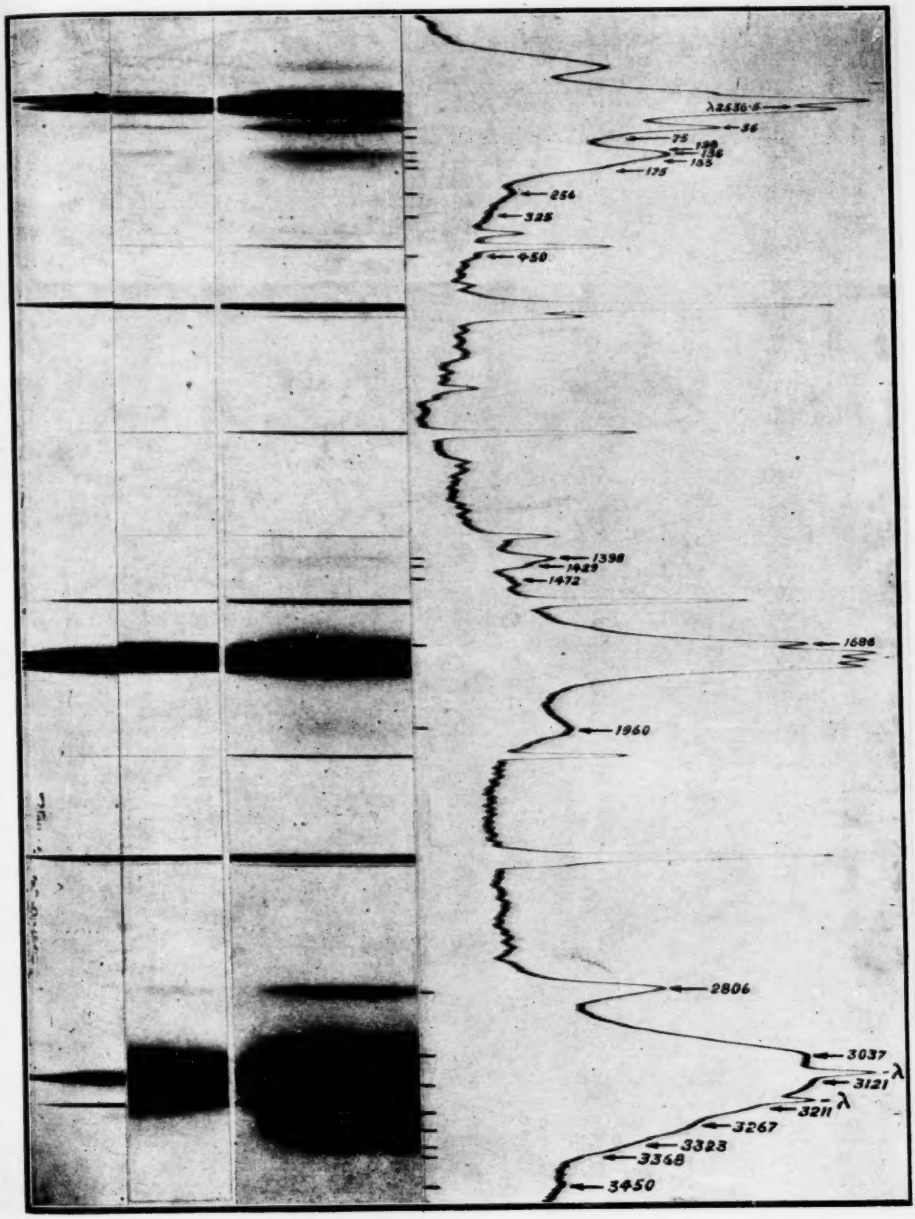
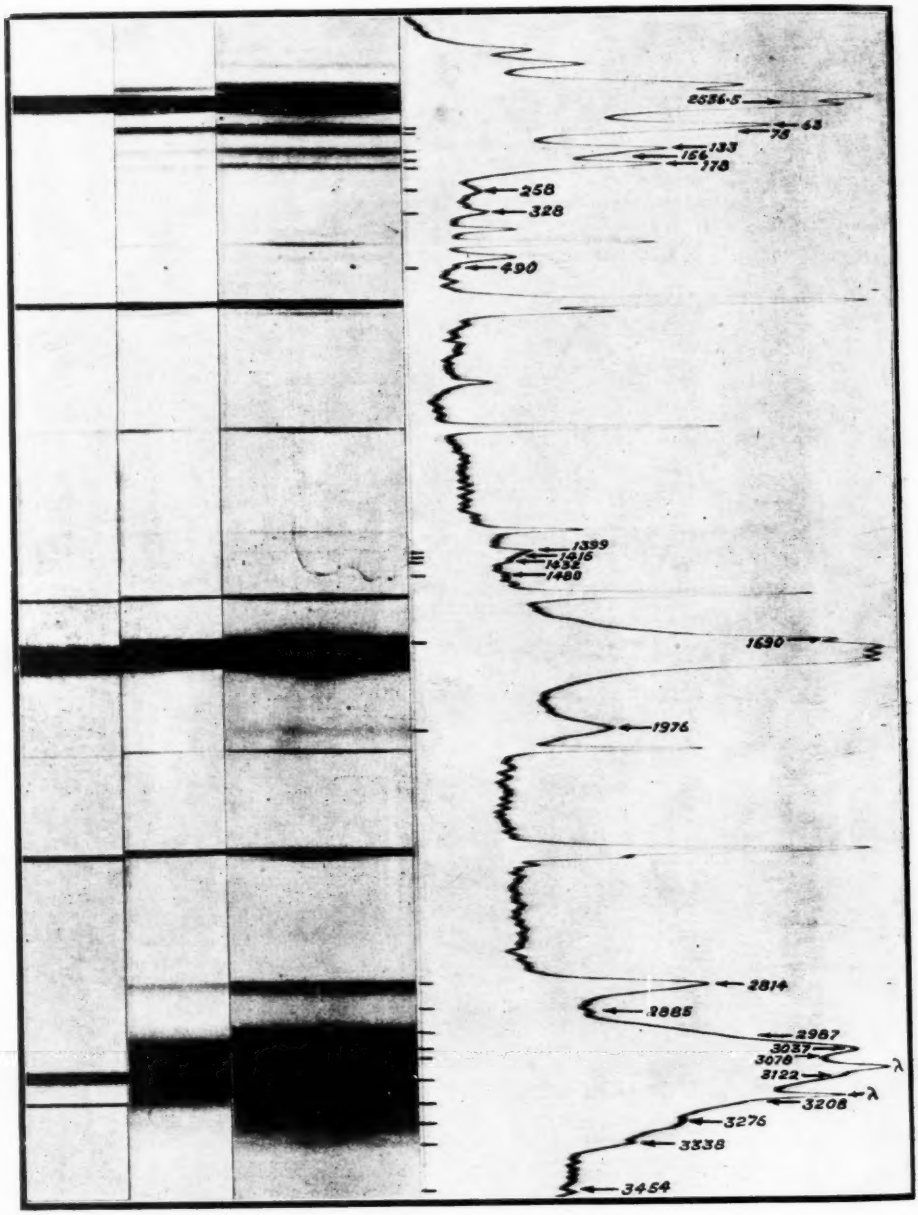

λ2536·5
56
75
135
175
254
325
450
1398
1429
1472
1686
1960
2806
3037
3121
λ
3211
λ
3267
3323
3348
3450
a
b
c
d

FIG. 1


2536·5
63
78
133
164
178
258
328
490
1399
1416
1432
1480
1630
1976
2814
2885
2987
3037
3078
3122
3208
3276
3338
3454
λ
λ

a b c d

FIG. 2

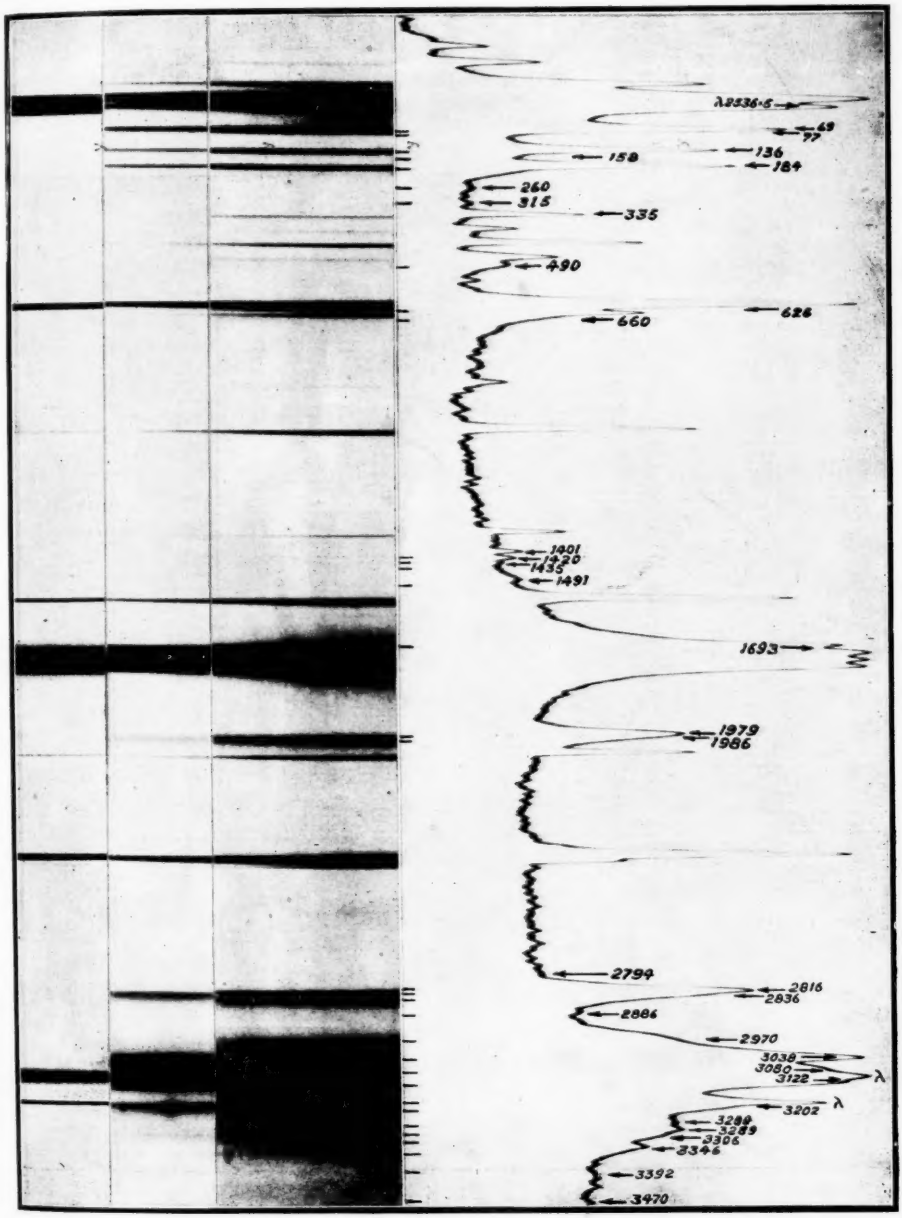

λ2536·5
49
77
136
158
184
260
315
335
490
626
660
1001
1420
1435
1491
1693
1979
1986
2794
2816
2836
2886
2970
3038
3080
3122
λ
3202
λ
3289
3289
3306
3346
3392
3470
a
b
c
d

FIG. 3

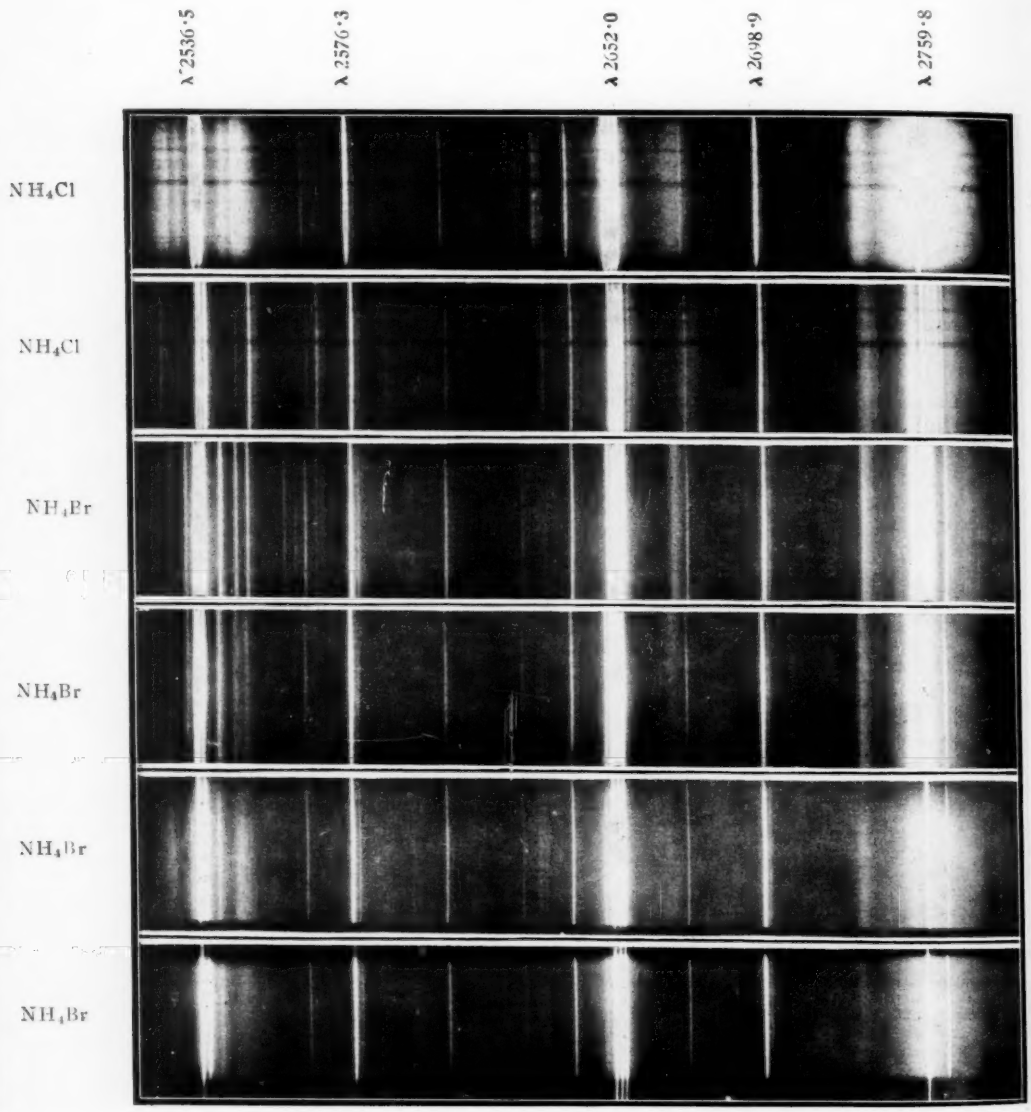

λ 2536·5
λ 2576·3
λ 2652·0
λ 2698·9
λ 2759·8
NH_4Cl
NH_4Cl
NH_4Br
NH_4Br
NH_4Br
NH_4Br

FIG. 4

Description of Plates

Plate V

Fig. 1. (*a*) Mercury spectrum taken with a Hilger medium quartz spectrograph,
(*b*) and (*c*) Prints of different depths enlarged from the same negative showing the Raman spectrum of ammonium bromide taken at 308° T.,
(*d*) its microphotometer record.

Plate VI

Fig. 2. (*a*) Mercury spectrum.
(*b*) and (*c*) Raman spectrum of ammonium bromide taken at 173° T.,
(*d*) its microphotometer record.

Plate VII

Fig. 3. (*a*) Mercury spectrum,
(*b*) and (*c*) Raman spectrum of ammonium bromide taken at 85° T.,
(*d*) its microphotometer record.

Plate VIII

Fig. 4. (*a*) to (*d*) Raman spectrum of ammonium bromide taken at four different temperatures.
(*e*) and (*f*) Raman spectrum of ammonium chloride taken at two different temperatures.

THE RAMAN SPECTRA OF CYCLOHEXANE, GLYCOL AND GLYCERINE

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1. Introduction

The Raman spectra of cyclohexane, glycol and glycerine have been studied by several authors with the λ 4358 radiation of the mercury arc as the source of excitation. Since these liquids are sufficiently transparent to the ultra-violet, it was of interest to investigate their Raman spectra excited by the intense λ 2536·5 radiations of a water-cooled magnet-controlled quartz mercury arc. The preliminary results obtained from such a study are reported in this paper.

2. Earlier Work

Cyclohexane.—The earliest study of the Raman spectrum of cyclohexane was made by Ganesan and Venkateswaran (1929) and Daure (1929). Krishnamurti (1931) was the first to observe as many as nineteen Raman lines in cyclohexane, but some of these lines were not confirmed by Wood and Collins (1932). Ananthakrishnan (1936) examined the spectrum with a spectrograph of large dispersion and reported the existence of about 21 lines. A calculation of the ring frequencies for cyclohexane was made by Saxena (1940) by the application of the methods of group theory. He also studied the polarization of the Raman lines and concluded that the C_6H_{12} molecule has a "chair" configuration, whereas Langseth and Bak (1940) have, from their studies, supported the planar configuration. Recently, Sutherland and Ramsay (1946) have calculated the frequencies of vibration of the carbon skeleton assuming a "chair" configuration for the C_6H_{12} molecule.

Glycol.—The Raman spectrum of glycol has been studied among others by Morris (1931), Martin (1931), Thatte and Shahani (1931), Howlett (1931) who could all observe only seven or eight prominent Raman lines. Kohlrausch and Koppl (1935) reported the existence of 12 Raman lines in glycol at $\Delta\nu = 342$, 478, 512, 862, 1033, 1059, 1086, 1258, 1457, 2709, 2866 and 2926 cm.$^{-1}$ So far, Ananthakrishnan (1937) has observed the largest number of lines in glycol which include lines at 900 and 1227 cm.$^{-1}$ in addition

to the above mentioned 12 lines. He has also studied the polarisation of the Raman lines.

Glycerine.—Bär (1933) was the first to observe about 14 lines in the Raman spectrum of glycerine while earlier workers (Ganesan and Venkateswaran, *loc. cit.*; Howden and Martin 1933; Carelli and Went, 1933, etc.) had reported only seven. A strong continuous spectrum was the chief obstacle in the way of these workers. Using a very carefully distilled sample of glycerine, Saxena (1935) was able to eliminate the continuous spectrum and reported the existence of many faint lines in the spectrum of glycerine in addition to those reported by Bär. He also studied the polarisation of the Raman lines and the effect of dilution.

3. Experimental

The experimental arrangements were essentially the same as those described in earlier papers by the author (1947, 1948). The liquids used for investigation were pure samples of Kahlbaum. Since the Raman lines were usually broad, a very fine slit about 0·025 mm. wide was used for photographing the spectra with a Hilger medium quartz spectrograph. An iron arc spectrum was usually superposed on the Raman spectrum to facilitate measurement of the shifts. The negatives were microphotometered with a Moll microphotometer.

4. Results

The frequency shifts of the Raman lines observed in the spectrum of cyclohexane, glycol and glycerine are classified in Tables I, II and III respectively. Intense spectrograms showing the main features observed in cyclohexane and glycol are reproduced in Figs. 1 and 2 respectively in Plates IX and X. Their microphotometer tracings are also reproduced in Plates IX and X. Reproducible spectrograms could not be obtained for glycerine.

Cyclohexane.—A wing of good intensity extending up to $\pm 95\,\text{cm.}^{-1}$ from the exciting line has been observed in the Raman spectrum of cyclohexane. This may easily be noticed in Fig. 1 in Plate IX. Considering the fact that the exciting radiation was efficiently filtered from the scattered light, there is no reason to doubt the genuineness of the wing.

New lines have been observed in the spectrum of cyclohexane. These are situated at $\Delta\nu = 475$, 527, 848, 896 and $1100\,\text{cm.}^{-1}$ The broad and intense line at $1445\,\text{cm.}^{-1}$ is seen to be made up of three components, namely, 1426, 1444 and $1463\,\text{cm.}^{-1}$ The Raman line at $2353\,\text{cm.}^{-1}$ reported by Ananthakrishnan has not been confirmed. With the dispersion of the

TABLE I. *Raman shifts observed in cyclohexane in cm.*$^{-1}$

Author	Ananthakrishnan	Langseth and Bak	Saxena
Wing ± 95			
384 (3)	384 (½)	384·1	382
425 (3)	426 (1)	427	428
475·5 (1)			
527·0 (½)			
	600 (0)		600
756·8 (0)		762	
802·0 (10)	802 (10)	801·7	802
848·0 (0)			
896·2 (0)			
1028·6 (8)	1029 (6)	1028·6	1029
1100 (0)			
1159 (6)	1156 (3)	1158·3	1156
1267 (8)	1265 (5)	1267	1265
1348 (5)	1348 (1)	1347	1348
1426·1 (1)		1426	
1444·0 (8b)	1442 (5b)	1445	1442
1463·0 (1)		1465·6	
	2353 (0)		
2461·9 (0b)	2467 (0)		2467
2604 (1)	2605 (0)		2605
2637 (2)	2630 (1)	2630	2630
2670·4 (3)	2662 (2)	2665	2662
2701 (2)	2698 (1)	2701	2695
2859 (8)	2853 (10b)	2853·8	2853
2894 (5)	2870 (1)		2883
2930 (6)	2888 (2)	2888·3	
	2898 (2)	2896·7	2922
2946 (6)	2922 (8)	2908·1	
	2937 (8)	2924·0	2937
		2934·7	

TABLE II. *Raman frequencies observed in Glycol in cm.*$^{-1}$

Author	Kohlrausch and Koppl	Ananthakrishnan
Wing ± 130		
344 (2b)	342	340 (1b)
476 (3)	478	475 (2)
509 (3)	512	520 (1)
698·4 (0)		
801·5 (1)		
865 (8)	862	865 (8)
884 (3)		900 (1)
1033·5 (6)	1033	1035 (2b)
1063·0 (6)	1059	1060 (2b)
1092·6 (5)		1090 (4)
	1086	
1133 (2)		
1224 (3)		1227 (½b)
1281 (5)	1258	1260 (3b)
1396 (1)		
1458 (8)	1457	1450 (8b)
2726 (2)	2709	2712 (1b)
2885 (10b)	2866	2860 (10b)
2932 (10vb) band	2926	2945 (10vb)
3250–3600		~3400 (2vb) band

TABLE III. *Raman frequencies observed in Glycerine in cm^{-1}*

Author	Bär	Saxena
		328 (1)
		370 (½)
420	427	419 (3)
488·6	497	489 (6)
544	553	546 (1)
	684	674 (2)
790	822	817 (3)
824	850	847 (6)
850		862 (2)
921	919	919 (5)
977	977	975 (2)
1051	1055	1048 (8)
		1085 (2)
1102	1108	1112 (5)
		1194 (1)
1246	1242	1246 (2)
		1309 (1)
		1378 (0)
1465	1471	1466 (8)
2737		
2889	2888	2880 (12)
2943	2947	2955 (12)
3392±200	3450	3202-3564
band	band	band

spectrograph used, it has not been possible to resolve the high frequency lines in the 2600–2940 cm.$^{-1}$ region into components observed by Anantha-krishnan.

Glycol.—It will be seen in Fig. 2, Plate X. that there is a wing accompanying the λ 2536·5 line on the Stokes and anti-Stokes sides. This wing although it is only of medium intensity extends up to $\pm$ 130 cm.$^{-1}$ from the Rayleigh line. The occurrence of such a wing has not been reported by earlier workers. The unique broadness of the Raman lines may be specially mentioned. The Raman lines at 698, 801, 884, 1133 and 1396 cm.$^{-1}$ are also reported for the first time. Of these the 884 and 1133 cm.$^{-1}$ lines are fairly strong while the others are weak. The main O–H band is found to extend from 3250–3600 cm.$^{-1}$

Glycerine.—One important result emerging from our study of glycerine is the fact that there is no wing accompanying the exciting line. It is interesting to note that while the wing is very intense in the monohydric alcohol CH_3OH (author, 1947), there is an appreciable reduction in the intensity of the wing in the dihydric alcohol $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ and there is no wing in the

spectrum of the trihydric alcohol—$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$

This indicates that in glycerine the molecules are more rigidly attached to their neighbours than in either glycol or CH_3OH.

Nearly all the Raman lines observed by Bär in glycerine are confirmed by the present study. Two new lines, one at 790 cm.$^{-1}$ and another at 2737 cm.$^{-1}$ have also been observed. As in glycol, the Raman lines in glycerine also are very broad.

The O–H band is quite prominent in both glycol and glycerine. It may be of interest to compare the position of the O–H band in various molecules having one or more O–H groups, *e.g.*, water, methyl alcohol, ethyl alcohol, glycol, glycerine which have all been studied by the present author under excitation by λ 2536·5 radiation.

Molecule		*Position of O–H band*
Water	H–OH	3260–3426–3610
Methyl alcohol	H. CH_2.OH	3200–3560
Ethyl Alcohol	H. CH_2. CH_2. OH	3200–3550
Ethylene glycol	OH. CH_2. CH_2. OH	3250–3600
Glycerine	OH. CH_2. CH (OH). CH_2. OH	3200–3600

The centre of the band is at about 3400 cm.$^{-1}$ in almost all cases.

In conclusion, the author wishes to express his heartfelt thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his keen interest in this investigation.

Summary

The Raman spectra of cyclohexane, glycol and glycerine have been investigated with the λ 2536·5 radiation of the mercury arc as exciter. The wing in cyclohexane is found to extend up to $\pm$ 95 cm.$^{-1}$ from the exciting line. Five new lines are also observed in the spectrum. Glycol exhibits a wing of medium intensity extending up to $\pm$ 130 cm.$^{-1}$ and some new Raman lines are reported in its spectrum. Glycerine does not show any wing at all.

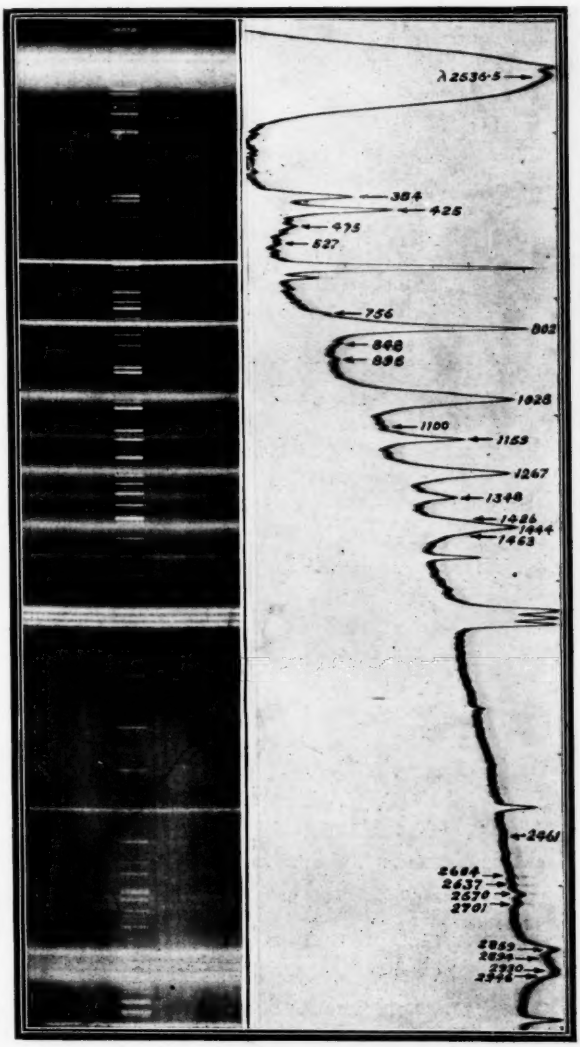

FIG. 1
Raman spectrum of Cyclohexane and its Microphotometer Record

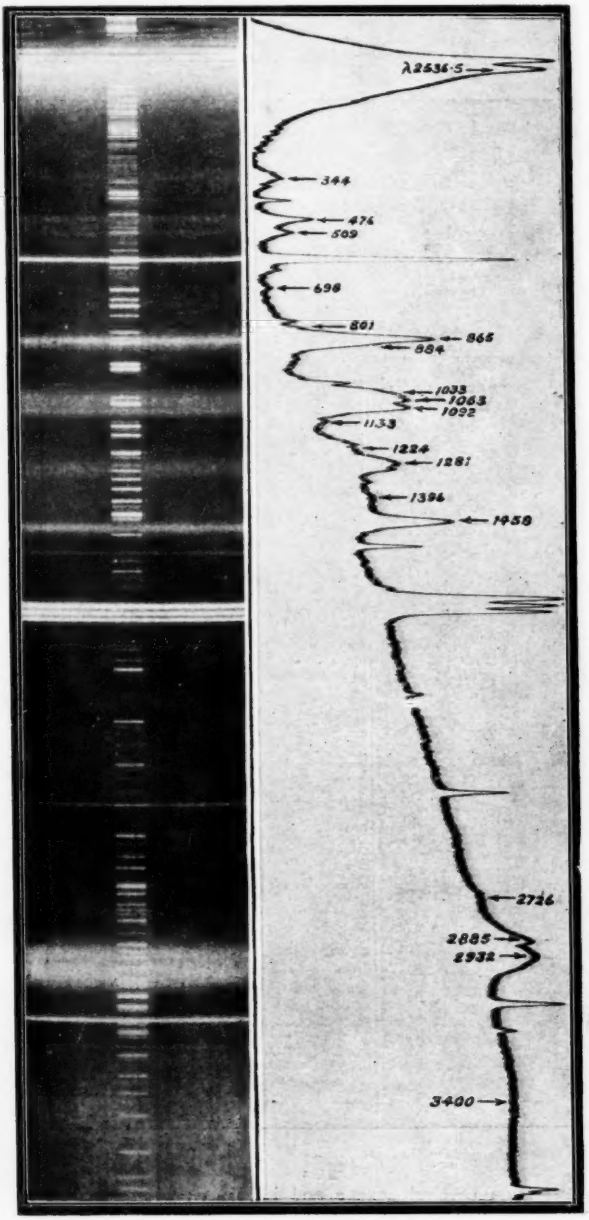

FIG. 2

Raman spectrum of Glycol and its Microphotometer Record

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CONTENTS

PAGE

A Note on the Formation of Quinones by Oxidative Demethylation and the Effect of Methylating Agents on Them . . . . . G. S. KRISHNA RAO, K. VISWESWARA RAO AND T. R. SESHADRI 245

A Note on the Constitution of Gossypitrin . . . . . V. V. SREERAMA MURTI AND T. R. SESHADRI 258

Synthesis and Study of 5:6:8-Hydoxy Flavonols . . . . . K. J. BALAKRISHNA AND T. R. SESHADRI 260

Sulphanilamides. Part I. Salts with Sulphonic Acids . . . . . S. K. MUNSHI, B. D. TILAK AND K. VENKATARAMAN 265

Monazite in the Beach Sands of Vizagapatam District . . . . . C. MAHADEVAN AND A. SRIRAMADAS 275

Some Observations on the Chemistry of Glycerides. Part I . . . . . A. R. SUKUMARAN KARTHA AND K. N. MENON 279

Formation of Complex Compounds between Lead Nitrate and Alkali Nitrates. Part I. The System: KNO_3—pb $(NO_3)_2$—H_2O . . . . . M. R. NAYAR AND C. S. PANDE 284

Formation of Complex Compounds between Lead Nitrate and Alkali Nitrates. Part II. The Systems: (a) $NaNO_3$-Pb $(NO_3)_2$-H_2O (b) KNO_3-$AgNO_3$-H_2O . . . . . M. R. NAYAR AND C. S. PANDE 293

Non-Association of Chemical Change with the High Frequencies in the Electrical Discharge . . . . . K. S. VISVANATHAN 300

The Raman Spectra of Water, Heavy Water and Ice . . . . . P. K. NARAYANASWAMY 311

Fluorescence and Phosphorescence of Diamond at Different Temperatures . . . . . V. CHANDRASEKHARAN 316

Raman Spectrum of Ammonium Bromide and Its Variation with Temperature . . . . . R. S. KRISHNAN 321

The Raman Spectra of Cyclohexane, Glycol and Glycerine . . . . . P. K. NARAYANASWAMY 336